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**LMH-1/HYDRAZINE HETEROGENEOUS
PROPELLANT DEVELOPMENT**

E. T. Niles, B. H. Seaman and E. J. Wilson

FINAL TECHNICAL REPORT AFRPL-TR-68-216

(16 MAY 1966 TO 18 OCTOBER 1968)

NOVEMBER 1968

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
EDWARDS AIR FORCE BASE, CALIFORNIA**

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(Prepared under Contract Nr. AF 04(611) - 11606 by
The Dow Chemical Company
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THE DOW CHEMICAL COMPANY
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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. AF 04(611)-11606. The contract was initiated under Air Force BPSN Nr. 623148, AFSC Project Nr. 3148, "LMH-1/Hydrazine Heterogeneous Propellant Development." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. G. Allen Beale as Air Force Project Officer.

This is the Final Technical Report, covering the work performed during the period of 16 May 1966 through 18 October 1968. The Dow Report Number is HZ-1A-68.

Management direction at Dow was under Mr. T. Houtman, Laboratory Director, and the work was supervised by Dr. J. C. Safranski, Jr., Laboratory Division Leader. Dr. E. T. Niles is the principal investigator with Mr. E. Wilson and Mrs. B. H. Seaman making major contributions.

Publication of this report does not constitute Air Force approval of report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

This technical report has been reviewed and is approved for publication.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division
Air Force Rocket Propulsion
Laboratory

(U) ABSTRACT

(U) In an integrated program, The Dow Chemical Company has developed a highly promising heterogeneous metallized propellant of LMH-1/ N_2H_4 which is stable, storable and has desirable rheological properties. Chemical stability and physical integrity, combined with ease of preparation, make this system especially attractive.

(U) The thermal stability and gas generation characteristics of LMH-1/ N_2H_4 formulations were studied and one year storability data were obtained. Major advances in LMH-1 technology have produced very substantial improvements in its stability. However, the stability of the best LMH-1 has been found to be further enhanced by propellant grade hydrazine. These formulations produce some initial gassing, followed by a very low gas generation rate. Pretreatment of LMH-1 with n-butylamine at controlled temperature and moisture conditions has been found to be effective in preventing initial gas generation and in long-term stabilization of LMH-1 in hydrazine formulations. A wide variety of gel and emulsions systems was investigated, which led to the selection of polyacrylamides for the heterogeneous system. This gelling agent, in combination with 40% LMH-1 and 60% hydrazine, produced a thixotropic heterogeneous propellant which exhibited a yield stress and retained excellent physical integrity under vibrational and gravitational forces. The cohesive propellant developed was found to possess engineering properties which are desirable in heterogeneous propellants. Fifty pounds of propellant were prepared and sent to the Air Force Rocket Propulsion Laboratory for Air Force in-house performance evaluation.

PROGRAM REQUIREMENTS

(U) The technical requirements of the program were:

(C) Phase I - to develop a heterogeneous aluminum hydride/hydrazine (40/60) system that has a total decomposition (mole percent hydrogen from aluminum hydride) less than 0.5% per year at 77°F with the desirable rheological properties as follows:

- (i) Cohesive but non-adhesive.
- (ii) Yield stress sufficient to withstand acceleration and vibration tests without separation.
- (iii) The apparent viscosity shall be less than 100,000 centipoise at 1 sec^{-1} and 500 centipoise at $10,000 \text{ sec}^{-1}$.

The investigation was to include the following:

- (i) Compatibility studies.
- (ii) Gelling and emulsifying agent screening.
- (iii) Study of heterogeneous system preparation parameters including:
 - a. Types and concentrations of thickening agents.
 - b. Aluminum hydride loadings.
 - c. Optimum method of preparation.
- (iv) System characterization including:
 - a. Density.
 - b. Apparent viscosity.
 - c. Yield stress.
- (v) Recommendation of system.

(U) Phase II - upon selection of a heterogeneous system meeting the requirements of Phase I, work was to be completed in the following areas:

- (i) Complete characterization including:
 - a. Flow curve - shear stress vs. shear rate.
 - b. Density vs. temperature - grams/cc. at 40°, 60°, 80°, and 100°F.
 - c. Storage stability at 77° and 120°F for one year.
 - d. Mechanical stability to the following requirements:

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1. Vibration stability:
 - a. Two hours at 5g peak sinusoidal vibration cycled over a range of 50 to 500 cps.
 - b. Ten minutes at 20g peak sinusoidal vibration at 500, 1000, and 2000 cps.
 - c. Temperatures for each test will be 40°, 80°, and 120°F.
 2. Acceleration stability:
 - a. One hour at 20g load.
 - b. Ten minutes at 90g load.
 - c. Temperatures for each test will be 77°F.
 - e. Minimum usable temperature.
 - f. Thermal stability from room temperature to boiling point.
- (11) Propellant supply.

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SECTION I

(U) INTRODUCTION

(C) The addition of high-energy solid particles, such as powdered metals and their hydrides, provides a promising method of increasing the performance of storable liquid propellants for rocket engines. This report summarizes a two-year research effort which resulted in the development of a heterogeneous aluminum hydride/hydrazine (40/60) system gelled with polyacrylamide that is stable, storable, and has desirable rheological properties. In addition, 50 pounds of the liquid heterogeneous propellant was furnished to the Air Force Rocket Propulsion Laboratory for performance evaluation. The research was divided into two phases. Phase I consisted of the development of a heterogeneous aluminum hydride/hydrazine propellant with specific properties, as discussed through Section III,A,2,b. Phase II involved the complete characterization and determination of one year storability data on the heterogeneous system (Section III,A,2,b through III,D,3,c).

(C) The term AlH_3 -1451 in this document refers to a stable crystalline phase of aluminum hydride.

SECTION II

(U) SUMMARY

(C) A two-phase research program was conducted which resulted in the development and characterization of a heterogeneous aluminum hydride/hydrazine (40/60) propellant. The most significant problems of thermal stability of the neat hydride and compatibility of the system components were overcome which provided a system that is stable and storable, and has desirable rheological properties. In addition, 50 pounds of propellant was prepared and sent to the Air Force (AFRPL) for evaluation.

(C) In Phase I a wide variety of gelling agents and surfactants were screened which led to the intensive study of four systems: (i) particulate gels with ammonium polyacrylates, (ii) acrylamide/acrylic acid copolymer gels, (iii) polyacrylamide gels, and (iv) emulsions based on oleyl sarcosine. The system chosen for characterization was the polyacrylamide gel at 0.5% with aluminum hydride/hydrazine (40/60). The formulation was found to be cohesive, and the cohesiveness could be controlled by the amount of crosslinking agent used in the polyacrylamide. The yield stress was sufficient to withstand acceleration and vibration tests without separation (700-1500 dynes/cm.²). The apparent viscosity was less than 100,000 centipoise at 1 sec⁻¹ and 500 centipoise at 10,000 sec⁻¹. The density of the heterogeneous propellant closely approaches the theoretical value. The system had a total decomposition of less than 0.5% per year at 77°F based on aluminum hydride present. The major advances in this respect were the discovery of the stabilizing effect of hydrazine on aluminum hydride and a pretreatment technique utilizing n-butylamine to reduce the initial gassing encountered in these systems. The method of preparation was also studied and found to be extremely facile with the polymeric gelling agents.

(C) In Phase II a complete characterization of the selected propellant system was accomplished. The characterization included determination of:

- (i) Flow curve
- (ii) Density vs. temperature
- (iii) Storage stability
- (iv) Mechanical stability (vibration and acceleration)
- (v) Minimum usable temperature
- (vi) Thermal stability

After one-year's storage, the total decomposition at 77°F was 874 cc./lb. or 0.395% for the propellant prepared with as-received hydrazine, and 590 cc./lb. or 0.267% for the gel prepared with distilled hydrazine. Gassing rate at one-year was 1.5×10^{-3} and 8.9×10^{-4} cc./lb./min. of propellant, respectively. The gassing rate of the propellant with as-received hydrazine was decreasing at the end of the test.

SECTION III

(U) TECHNICAL RESULTS AND DISCUSSIONA. AGENT SCREENING AND SYSTEM DEVELOPMENT (U)

(C) Research to develop a stable, storable, heterogeneous $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ propellant with desirable rheological properties was conducted in an integrated program to furnish a thickened system and to study the compatibility of the system components. The major requirement for an acceptable propellant was that the decomposition rate of the heterogeneous $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ (40/60 weight percent) system had to be less than 0.5% per year (calculated as mole percent hydrogen evolved from $\text{AlH}_3\text{-1451}$) when stored at 77°F. The desired rheological properties of the propellant were as follows:

- (i) Cohesive but non-adhesive.
- (ii) Yield stress sufficient to withstand acceleration and vibration tests without separation.
- (iii) Apparent viscosity less than 100,000 centipoise at 1 sec.⁻¹ and 500 centipoise at 10,000 sec.⁻¹.

(C) Two types of thixotropic systems were investigated: gel and emulsion. Polymeric gelling agents were screened with hydrazine to study the effect of the combination of functionality, molecular weight and degree of crosslinking to produce an optimum, cohesive gel. Emulsifying agents were screened to determine systems which would produce water in oil (W/O) type emulsions and be stable with $\text{AlH}_3\text{-1451}$.

(U) Three gelled and one emulsion systems were selected from the screening program as prime candidates for the propellant. The gelling agents were polyacrylamides, acrylic acid-acrylamide copolymers and ammonium polyacrylates. The emulsifier was a hydrazine derivative of oleyl sarcosine with decane as the external phase. After more comprehensive studies of the rheological properties and physical integrity of the candidate systems. The gelled propellant prepared with polyacrylamide was chosen for development and characterization.

1. Gels (U)

(U) A variety of gelling agents which produce cohesive water gels was evaluated during the screening program to determine if 0.5 to 1.0% mixtures of the agent with hydrazine were cohesive, non-adhesive, viscous, shear-thinning and compatible (see Appendix A.I). A group of commercial and experimental agents was emphasized, in particular polyacrylamides, acrylic acid-acrylamide copolymers and ammonium polyacrylates. Each of the three gelling agent types listed produced gels with adequate physical properties, but the polyacrylamide was the least sensitive to atmospheric exposure. Thus, as a result of close coordination between research teams, a polyacrylamide gelling agent was tailor-made to give optimum cohesive properties to the heterogeneous gels.

a. Polyacrylamides (U)

(U) The best hydrazine gel properties were produced by polyacrylamide gelling agents with extremely high molecular weight, low crosslink density and low degree of hydrolysis. Slight changes in the amount of crosslinking agent (a few parts per million), the molecular weight and the degree of hydrolysis in the gelling agent influence the rheology of the heterogeneous system. With polymers in the 10-20 million molecular weight range, the gel structure can accommodate large volumes of hydrazine to produce an adhesive gel. However, as the number of crosslinks is increased, the capacity of the gel is decreased and the gel becomes more cohesive.

(U) When it was discovered that slight variations in crosslink density changed the adhesive-cohesive properties, a series of polyacrylamides with different amounts of crosslinking agent was prepared. The polymers and the cohesion of their hydrazine gels are evaluated in Table I. The gel with the uncrosslinked polyacrylamide was very adhesive; however, a polymer with a low level of crosslinking agent formed a cohesive gel. As a result of those experiments, polyacrylamide gelling agents similar to ST-475-10-133B were selected for further study.

Table I

(U) Polyacrylamide Gelling Agent Analysis

<u>Agent</u>	<u>Cross-linker</u>	<u>Cohesion</u>
ST-475-10-133F	0	Adhesive
ST-475-10-133A	X ^a	Good
ST-475-10-133B	2X	Good
ST-475-10-133C	5X	Adhesive
ST-475-10-133D	10X	Poor
ST-475-10-133E	15X	Poor

^aThe lowest initial concentration of the crosslinking agent is represented by the symbol X.

(U) Polyacrylamides can be prepared with varying degrees of hydrolysis, i.e., some of the -C-NH₂ groups are hydrolyzed to

$\begin{array}{c} \text{O} \\ || \\ \text{-C-OH} \end{array}$ Early in the program a low degree of hydrolysis was found desirable, and the majority of the work was conducted with polyacrylamides which were about 0.05% hydrolyzed. It is known that water gels prepared with polyacrylamides can break down somewhat under slightly acidic conditions; they are stabilized under basic conditions. Thus, hydrazine should afford a stabilizing medium for polyacrylamides, which indeed has been observed in this research effort.

b. Acrylic Acid-Acrylamide Copolymers (U)

(U) Screening data showed that polymer structure of the acrylic acid-acrylamide copolymers controlled the gel properties in much the same manner as was described for the polyacrylamide gelling agents. In one series of agents that was screened, the amide/acid ratio was varied and no crosslinking agents had been added. The results of the screening tests with hydrazine are listed in Table II, ST-475-6-110 series. Gels did not form with hydrazine until the amide/acid ratio in the copolymer exceeded 1.0, which indicated that a low degree of acid function was necessary for optimum gels. In the second group listed in Table II, ST-475-9-38 series, the ratio of amide/acid was held at 1.5 and the amount of crosslinking agent was increased incrementally. The least crosslinking produced the most promising gels. Thus, a new series of agents/acrylamide/acrylic acid copolymers (60:40) was prepared. The amount of crosslinking agent was varied at a low percentage range to produce the series of gelling agents presented in Table III. The table includes the initial gelled hydrazine screening results. These data illustrate, once again, that the amount of crosslinking agent is critical to the over-all physical properties of the gel. As the amount of crosslinking agent is increased, the resulting gel becomes more cohesive and exhibits greater stability.

(C) The screening experiments were repeated with the addition of 40% AlH_3 -1451 to the mixes. Three of the agents, ST-475-10-48C, ST-475-10-48D and ST-475-10-48E, maintained their cohesive properties although the mixes were dry and stiff. When the agent concentration was lowered to 0.3%, the gel thinned only slightly. However, the particles of gelled hydrazine adhered to each other and did not uniformly coat or provide a matrix for the heterogeneous phase, i.e. the AlH_3 -1451 was excluded from the gel phase. The gelled hydrazine formed into large, clear particles. Gel texture was found to be a function of the initial particle size of the gelling agent. The copolymer, ST-475-10-48C, was sized and heterogeneous gels were prepared. The gelling agent fraction below 150 μ with 0.42% agent produced a smooth gel with the AlH_3 -1451 included in the gel mixture, which could be easily extruded through a Nr. 15 hypodermic needle. The yield point of this mixture was found to be about 615 dynes/cm.². A similar mixture with 0.21% gelling agent yielded at 560 dynes/cm.². A density of 1.13 g./cc. was measured for these mixtures with 40% AlH_3 -1451. A heterogeneous gel with AlH_3 -1451, Lot Nr. 08126, was stable during storage at ambient temperature for 57 days before slight syneresis was observed.

c. Polyacrylates (U)

(U) Sodium and ammonium salts of extremely high molecular weight polyacrylic acids were supplied for this program by the Texas Division of The Dow Chemical Company. The ammonium polyacrylates are in a bead form which, in the presence of hydrazine, swells to a cohesive, "fish egg" mass that does not adhere to the sides of the container and is shear thinning. The sodium polyacrylates, also in bead form, do not gel hydrazine.

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Table II

(U) Screening Results for Acrylamide/Acrylate Copolymers

Agent	Agent Concentration wt. %	Ratio Amide/Acid	Added Crosslinker	Gel Characteristic	Stability 24 hrs. @50°C.	Remarks
ST-475-6-110A	0.5	10/90	0	No gel	--	--
ST-475-6-110C	0.5	50/50	0	No gel	--	--
ST-475-6-110D	0.5	76/24	0	Adhesive	No change	--
ST-475-6-110E	0.5	90/10	0	Adhesive	Thinned	--
ST-475-9-38A	0.5	60/40	4X ^a	Cohesive	No change	Effective to 0.25% agent
ST-475-9-38C	0.5	60/40	20X	Cohesive	--	Thin at 0.25% agent
ST-475-9-38B	0.5	60/40	40X	Cohesive	--	Thin at 0.25% agent

^aThe lowest initial concentration of the crosslinking agent is represented by the symbol X.

Table III

Screening Results for Acrylamide/Acrylic Acid Copolymers (U)

Copolymer Agent	Agent Concentration %	Added Cross-linker	Gel Characteristics	Stability, 24 hrs. at 55°C.
ST-475-10-48F	0.5	0	Adhesive	Thinner
ST-475-10-48A	0.5	X ^a	Sl. adhesive	Broken
ST-475-10-48B	0.5	2X	Sl. adhesive	Broken
ST-475-10-48C	0.5	5X	Cohesive	Sl. thinner
ST-475-10-48D	0.5	10X	Cohesive	No change
ST-475-10-48E	0.5	15X	Cohesive	No change

^aX represents the initial concentration of the crosslinking agent.

(U) Several series of ammonium polyacrylates were screened to determine the optimum gelling agent structure, i.e. combination of molecular weight and amount of crosslinking agent, since slight changes in these structural variables affect the hydrazine capacity of the gelling agent, the adhesive-cohesive properties of the gel and the rheology of the heterogeneous system. These properties are actually related to crosslink density; however, since molecular weight of the ammonium polyacrylates cannot be determined, the crosslink density cannot be calculated. A qualitative evaluation of the molecular weights can be made by comparison of the hydrazine gel capacity (g. of hydrazine/g. of agent) and the amount of crosslinking agent. The gel capacities of three series of polyacrylates are presented in Table IV. Series A and B are higher molecular weight polymers than Series C. The gel capacity decreases within each series with increased crosslinking agent.

(C) Series A and B produced "dry" heterogeneous gel mixes with 40% AlH₃-1451 and 0.42% gelling agent, because of the extremely high gel capacities. The C series of polymers produced heterogeneous gels with good properties, but gels prepared from the higher crosslinked members were subject to syneresis.

(C) Small samples (30 g.) of heterogeneous propellants containing AlH₃-1451 (Lot No. 08126)/hydrazine (as received) 40:60, were prepared to compare the properties of selected ammonium polyacrylates.

(C) The heterogeneous propellants were prepared by first combining the AlH₃-1451 and hydrazine, and stirring for about 3 minutes to wet the hydride. Next, the agent was added and the mixture was stirred until it gelled. The hydride, Lot Nr. 08126, was off-grade hydride (less than 12 days to 1% decomposition at 60°C.) which had been washed twice with hydrazine and dried under vacuum.

Table IV

Hydrazine Gel Capacities of Ammonium Polyacrylates (U)

<u>Series</u>	<u>Polyacrylate Agent Tex-B</u>	<u>Concentration of Crosslinker</u>	<u>Gel Capacity, g. N_2H_4/g. agent</u>
A	1008.20	2X ^a	1280
	1008.21	4X	1016
	1008.22	6X	1060
	1008.23	8X	500
B	1008.24	X	1100
	1008.25	3X	1088
	1008.26	4X	350
	1008.27	5X	550
C	1008.15	4X	Soluble
	1008.16	6X	431
	1008.17	8X	493
	1008.18	10X	373
	1008.19	12X	251

^aX represents the initial concentration of the crosslinking agent.

(U) The preparation characteristics and properties of the ammonium polyacrylate heterogeneous propellants are presented in Table V. The best over-all properties were obtained with Tex-B 1008.15. In general, the heterogeneous gels prepared with ammonium polyacrylates have a short shelf life; between 16 and 22 days after preparation the Tex-B 1008.15 gels break. The shelf life varies from lot to lot of hydride, which indicates that slight changes in purity of surface characteristics of the hydride affect the long-term physical properties of the gel. Ions carried along with the hydride most likely affect the gel structure. Thus, hydride type and pretreatment is extremely important with the ammonium polyacrylate gels.

d. Gelling Agent Screening Parameters (U)

(U) During the screening program several properties were compared for the most promising gelling agents and two established gel systems, powdered aluminum with Carbopol 940 and with the combination of carboxymethyl cellulose (4)/agar-agar (1). The parameters for each gelling agent system are listed in Table VI. A discussion of the parameters follows.

Table V

(C) Characteristics and Properties of Ammonium Polycrylate and Acrylic Acid-Crylate Copolymers with Various R₁ and R₂

Agent	Conc., %	Gel Time, min.	Coagulation	Ease of Shear	Flow	Syringe Extrusion	Centrifuge 10 min. at 180 g.	Density g./cc.	Yield Stress, dynes/cm. ²	Storage Stability
Tex-B 1008.9	0.35	3	V. Good	Good	None	Difficult	No separation	1.103	---	Syneresis @ 7 days
Tex-B 1008.15	0.42	2	Good	Pair	Slight	Good	Sl. separation	1.105	503	Broke @ 22 days
Tex-B 1008.17	0.42	4	Good	Good	Slight	Difficult	--	--	---	Syneresis @ 1 day
Tex-B 1008.17	0.35	4	Good	Good	V. Slight	Good	No separation	--	1642	Dry @ 7 days
Tex-B 1008.20	0.35	5	V. Good	Poor	None	Difficult	Separation	1.23	---	Syneresis @ 1 day
Tex-B 1008.26	0.30	4	V. Good	Poor	None	Difficult	Separation	1.14	1651	Syneresis @ 1 day
Tex-B 1008.22	0.42	2	Good	Pair	Slight	Difficult	--	1.13	961	Syneresis @ 15 days
Tex-B 1008.31	0.30	8	Poor	Poor	None	Difficult	Separation	1.19	---	Broke @ 4 days
Tex-B 1008.28	0.31	3	Good	V. Good	Slight	Good	--	1.19	---	Broke @ 3 days
ST-475-10-48 ¹	0.42	2	Good	Good	Slight	Good	Sl. separation	--	467	Broke @ 57 days
ST-475-10-48 ²	0.42	2	Good	Good	Slight	V. Good	separation	1.074	1473	Broke @ 16 days
4 CMG/1 Agar-Agar	0.42	16 hrs.	Adhesive	Pair	Slight	V. Good	Sl. separation	--	1624	Gassed @ 5 days
Tex-B-1008.15/ ST-475-10-48 ¹ (4:1)	0.42	1 min.	Good	Good	V. Slight	V. Good	No separation	--	1511	---

¹Stored at ambient temperature

²Stored at 60°C., accelerated aging

Table VI

(U) Properties of Selected Heterogeneous Propellant Formulations

Parameter	Ammonium Polyacrylate	Acrylic Acid- Acrylamide Copolymer	Polyacryl- amide	CMC(4)/ Agar-Agar(1)	Carbopol 940
COMPOSITION $\text{N}_2\text{H}_4/\text{AlH}_3$ -1451	60:40	60:40	60:40	60:40 A1	57:43 A1
Additive, wt. %	0.42	0.42	0.42	0.42	0.42
COHESION	V. Cohesive	Cohesive	Cohesive	Cohesive	Adhesive
PHYSICAL INTEGRITY 25°C.	Fair	Good	V. Good	Fair	V. Good
60°C.	Poor	Fair	Good	--	--
ACCELERATION STABILITY	Good	Good	V. Good	--	V. Good
SENSITIVITY TO ATMOSPHERE	Poor	Fair	Good	Fair	Poor
GEL TIME, MIN.	2	2	3	150-180.	240-360.
DENSITY, g./cc. at 25°C.	1.07	1.11	1.16	1.37	1.42
YIELD STRESS, dynes/sq. cm. @ 25°C.	700-900	500-600	600-800	1180	1400-2200

(U) 1. Cohesion - Special attention was paid to the cohesive-adhesive properties of the gels during screening, since a cohesive, non-adhesive gel is needed to avoid excessive hold-up on container walls during propellant handling. The gels were evaluated for tendency to stick to both the glass container walls and a metal spatula. The candidate gels were all adequately cohesive.

(U) 2. Physical Integrity - Gels were observed for syneresis and periodically tested for yield stress during storage at 25°C and at 60°C. Gels with polyacrylamide were superior in shelf-life tests with very little physical changes during storage.

(C) 3. Acceleration Stability - Ten-gram gel samples were centrifuged for 10 minutes with 180 g acceleration at 77°F. The samples were inspected visually for separation of liquid, clear gel or solid AlH_3 -1451. All of the gel systems passed this test adequately with the polyacrylamide again considered superior.

(U) 4. Sensitivity to Atmosphere - Brief exposure to air was detrimental to all of the gels except the polyacrylamide system, which experienced contact with atmospheric conditions for 5-6 hours with no evidence of syneresis or other detrimental effects.

(C) 5. Gel Time - The time required to gel the hydrazine sufficiently to suspend the solid AlH_3 -1451 in the gel matrix was observed. All the candidate gels thickened within minutes after the hydrazine and gelling agent were combined. The polyacrylamide gelled somewhat slower than the ammonium polyacrylates and the acrylic acid-acrylamide copolymers and was thus considered the most workable system for preparing a uniform gel in a reasonable length of time.

(C) 6. Density - The density of the gel systems was measured at 25°C with an air comparison pycnometer. All the systems were near the theoretical value of 1.16 g./cc. with the polyacrylamides approaching most closely.

(C) 7. Yield Stress - The yield stress of the gels was measured with a capillary yield stress apparatus which is described in Appendix C. The yield stress of the gels could be controlled by the amount of gelling agent present and was adequate to suspend the solid AlH_3 -1451 in all cases.

(U) 8. Other Observations - Three empirical tests that are not listed in Table VI were performed in early screening work to evaluate gels. The shear thinning properties of gel systems were estimated by passing a metal spatula through the gel mass and observing the ease of shear. Shear thinning was also estimated by extruding the gel through a Nr. 15 syringe needle and noting ease of shear, and cohesiveness. Yield stress was estimated roughly by the tendency of the gel to flow or remain stationary under the force of gravity.

(U) In the majority of the tests the three gel system candidates were adequate, but the polyacrylamide gels were superior in most cases.

2. Emulsions (U)

(C) High internal phase emulsions tend to exhibit thixotropic rheology. Such emulsions with solid loading were investigated in the development of a heterogeneous propellant system of hydrazine with aluminum hydride. Decane was chosen as the external phase of the emulsion in the initial screening of a wide variety of commercially available emulsifying agents. Later development work included fuel oil, kerosene, and jet fuel as the external phase. A new emulsifier, OSH, was developed which produces emulsions of anhydrous hydrazine and decane loaded with AlH_3 -1451 that are stable at room temperature. The emulsions have the desired rheology and are chemically compatible, but are adhesive and sensitive to temperature cycling.

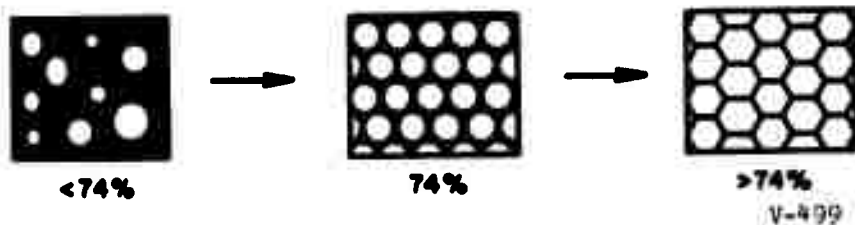
a. High Internal Phase Emulsions (U)

(U) The more common emulsion systems consist of an oil-like material as the disperse internal phase and water as the continuous external phase held in that configuration by an emulsifier. The oil is present as spherical droplets of varying size. This description holds for the classical emulsions in which the disperse internal phase is 20-70% by volume and the continuous external phase is the corresponding 80-30%. The physical properties of such an emulsion are largely determined by the external phase.

(U) As the internal phase approaches and becomes greater than 74% by volume, the geometry of the system causes pronounced effects on physical properties and stability of the emulsion (see Figure 1). The internal phase droplets have room for random motion when the internal phase is below 74%; however, at 74% internal phase, the droplets become close packed spheres, each of which contacts 12 other spheres which restricts movement somewhat. Any increase of internal phase over 74% changes the emulsion markedly. The droplets flatten at their points of contact and approximate dodecahedrons as the internal phase increases. The polyhedron configuration restricts movement and the viscosity increases sharply. Considerable energy is required to create the greater surface area. At or near 74% internal phase, the emulsion tends to break into two separate liquid phases or invert to the opposite type of emulsion to give 26% internal phase and 74% external phase, unless a surfactant stabilizes the emulsion sufficiently to prevent separation of phases. With emulsions of high percentage internal phase, the choice of emulsifying agent and mixing conditions becomes critical, if a stable emulsion is desired.

(C) In contrast to the more common oil in water (O/W) emulsions, the target for this contract was a water in oil (W/O) type emulsion which approached the extreme conditions of the close packed dodecahedron arrangement with the internal phase approximately

90% by volume. For screening purposes, the total heterogeneous propellant formulation was composed of a W/O emulsion of anhydrous hydrazine as the internal "water" phase and decane as the external "oil" phase with a solid loading of AlH₃-1451.



(U) Fig. 1 - Schematic Representation of Emulsion Appearance under Microscope for Given Internal Phase Percentages as Noted

b. Screening Program (U)

(U) The inherent characteristics of each emulsion system place specific requirements on the choice of emulsifying agents for the system. For the hydrazine-decane combination, the specifications become especially stringent. (See Appendix A.II. for a list of emulsifying agents screened during the program.)

(1.) W/O Emulsions (U)

(U) Initial screening of 72 selected surfactants was begun by experimentally estimating the hydrophile-lipophile balance, HLB. The HLB values act as a measure of the balance between the attraction for water or for oil of the various functional groups in the surface active agent. The suitability of an agent for a specific application can be determined with HLB numbers. Table VII shows that the HLB range of suitable agents which produce aqueous W/O emulsions is much more limited than for aqueous O/W emulsions. Hydrazine emulsions would be expected to have a similarly narrow HLB range for W/O type emulsions.

Table VII

(U) HLB Ranges and Their Application

<u>Range</u>	<u>Application</u>
3-6	W/O emulsifier
7-8	Wetting agent
8-18	O/W emulsifier
13-15	Detergent
15-18	Solubilizer

(U) Agents were selected for screening chiefly on the basis of their known solubility in kerosene or oil. Of the 72 chosen for screening, only 21 tested in the 3-6 HLB range.

(U) The method of estimating HLB range was that described by Becher (1) (Table VIII). Methods to calculate HLB are known, but were impractical in this work.

Table VIII

(U) Approximation of HLB by Water Solubility

<u>Behavior When Added To Water</u>	<u>HLB Range</u>
No dispersibility in water	1-4
Poor dispersion	3-6
Milky dispersions after vigorous agitation	6-8
Stable milky dispersion (upper end almost translucent)	8-10
From translucent to clear dispersion	10-13
Clear solution	13+

(U) Since appropriate HLB range did not guarantee that the material would be soluble enough in anhydrous hydrazine or decane to form an emulsion, it was not surprising that several of the 21 promising surfactants proved to be unsuitable. About 15 agents remained candidates for the system after screening by HLB and solubility in N_2H_4 or decane (see Appendix A.II.).

(2.) Emulsion Stability (U)

(U) Possible emulsion stability was checked roughly by an empirical test to determine the spreading coefficient, S , between anhydrous N_2H_4 and decane solutions of various agents. The spreading coefficient can be calculated in some cases, but, again, calculations were impractical for this application. Candidates for the most stable emulsion formation were determined experimentally by observing the tendency of one liquid to spread on the surface of another.

(U) If a drop of hydrazine spreads on the surface of a decane solution of emulsifier, S is positive and emulsion stability would be very poor. If the hydrazine droplet forms a spherical bead on the surface of the decane solution, S is zero or negative and a stable emulsion is possible. O/W emulsions are most stable when S is slightly negative. For W/O emulsions the most stable conditions are met with the most negative coefficient possible that is still consistent with a low interfacial tension. This condition can be observed when several beads of hydrazine are suspended on the surface of an emulsifier solution in contact with each other, but show no tendency to coalesce. With that specific emulsifier,

an emulsion droplet of hydrazine could migrate to the surface of the emulsion and remain a spherical droplet, rather than spread on the surface and promote separation of the liquid phases.

(C) In several cases during the screening program, observation of spreading phenomenon was masked by N_2H_4 fumes or by a solid reaction product between N_2H_4 and the emulsifier. For the several agents with negative spreading coefficients, the HLB range indicated that emulsifiers in the HLB range of 3-4 could form stable emulsions with the anhydrous N_2H_4 -decane system. In the screening program the emulsifier with the most negative coefficient indeed produced a stable emulsion.

(3.) Anhydrous Conditions (U)

(U) Emulsions containing anhydrous N_2H_4 present special problems that are seldom encountered with aqueous emulsions. Most evaluations of emulsifiers are based on their behavior with water. Since hydrazine is a non-aqueous solvent, assumptions based on analogies to water can be misleading. Many surfactants are commonly used with water, and complete drying is unnecessary for ordinary use. Indeed, some products can contain as much as 50% water. Also, because of their hygroscopic nature, some agents are difficult to keep anhydrous. Since water in the complete system must be limited to 1% or less, the water content of any promising emulsifiers must be carefully controlled.

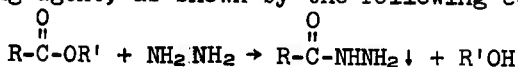
(U) A series of four Hodag C-100 amines was investigated. The oleic, lauric, stearic and tallic derivatives formed emulsions with anhydrous hydrazine and decane. In the as-received condition, the stability of the emulsions was in decreasing order of the emulsifiers as named. All of the emulsifiers lost about 10% volatiles when dried. The dried materials produced emulsions of limited stability with undistilled hydrazine (water content 0.8%). With distilled hydrazine the dried surfactants either formed no emulsion or an emulsion that separated in a few minutes. The undried emulsifiers accelerated the decomposition of hydrazine, as observed by gas formation in aged homogeneous emulsions.

(U) Since the water in the imidazoline derivatives was incompatible with as-received hydrazine, and because drying apparently altered the spreading coefficient and/or HLB of the emulsifiers, the Hodag C-100 amines were unsuitable for storable hydrazine emulsions.

(4.) Reactivity (U)

(U) The chemical reactivity of anhydrous N_2H_4 is again very different from that of water. Hydrazine acts as a strong reducing agent, can undergo reaction with other compounds, and can be neutralized as a base to form salts.

(U) The chemical reactivity is illustrated graphically in the case of organic esters which can produce W/O emulsions of N_2H_4 . In the presence of esters, N_2H_4 and decane readily form W/O emulsions. However, the emulsions break after brief aging, because hydrazine forms an insoluble hydrazide and destroys the emulsifying agent, as shown by the following equation:



(U) Insoluble hydrazides were recovered from hydrazine/decane emulsions that contained esters as emulsifying agents. The reaction products were identified by infrared analysis. A carbonyl shift from 5.75μ to $6.1-6.5\mu$ indicated loss of the organic ester and formation of the hydrazide.

(U) Several other surfactants were incompatible with hydrazine, but not all of the reactions were fully characterized. Sulfonates apparently reacted with hydrazine and produced insoluble products. One amine (polyoxyethylene oleylamine) formed a good W/O emulsion, but the mixture gassed as it aged, which could have been N_2H_4 decomposition, if the amine emulsifier was contaminated with trace amounts of heavy metals. However, all surfactant reactivity was not detrimental. An organic acid surfactant (Sarkosyl O, oleyl sarcosine) reacted with hydrazine to form a unique emulsifier for the hydrazine/decane system which is discussed in Section III,A.2.d.).

c. Other Emulsifiers (U)

(U) Twelve samples of emulsifiers were obtained from AFRPL. The surfactants were screened for ability to emulsify anhydrous hydrazine with decane. The screening results are listed in Appendix B.

(U) Solubilities of the samples in water, hydrazine and decane were checked, and the HLB values and spreading coefficients were estimated. The majority of the materials appeared to be organic esters as indicated by infrared spectra. Previous experience with organic esters has indicated that these materials can decompose in the presence of anhydrous hydrazine with subsequent loss of emulsion stability.

(C) H-4426A and H-4364 formed very viscous emulsions of hydrazine and decane which thinned upon aging. The homogeneous emulsions were prepared with 2.5% emulsifying agent, 5.8% decane and 91.7% anhydrous hydrazine. The hydrazine was added incrementally to the decane-emulsifier solution. Because of the difficulty of mixing the last few increments of hydrazine, emulsions of the composition appeared to be at the limit of internal phase capacity. Upon standing, the emulsion exuded hydrazine. The presence of excess hydrazine prevented adhesion to the container, but also seemed to promote coalescence of the emulsion droplets and thinning of the emulsion. When AlH_3 -1451 was added to the homogeneous emulsions, the mixture became adhesive.

(U) Fuel oil was used as the external phase with H-4426A to produce a waxy, extremely viscous emulsion. The internal phase capacity was considerably reduced and about one quarter of the hydrazine remained unmixed. Upon aging, the consistency changed radically. The excess hydrazine was taken into the emulsion which was very thin.

(U) The surfactant samples lose about 8-11% of their original weight upon drying in vacuo. The emulsifying properties do not appear to be altered, but the compatibility with hydrazine is increased as observed by reduced gas evolution in the aged emulsions.

(U) Since the consistency of hydrazine emulsions with these emulsifiers apparently changes upon aging, their value as reference standards is in question. Freshly mixed emulsions possibly could be used to obtain relative values for physical property measurements to compare with the work of others on heterogeneous emulsions.

d. Emulsion Development (U)

(C) Emulsion development was concentrated upon hydrazine decane emulsions prepared with a reaction product of oleyl sarcosine and hydrazine, which will be referred to as OSH emulsifier. Attempted characterization of OSH emulsifier only partially identified the structure of the material, but did not prevent optimization of the emulsion system. Emulsions with and without AlH_3 -1451 were prepared and evaluated by a series of tests. The optimum heterogeneous system with AlH_3 -1451 was acceptable on all points, except temperature cycling sensitivity and adhesiveness, which eliminated all emulsions as candidates for the systems of choice for scale-up and characterization.

(1.) OSH Emulsifier (U)

(C) Oleyl sarcosine (Sarkosyl O from Giegy Industrial Chemicals) in the as-received condition does not form a W/O emulsion of hydrazine and decane, but, after sufficient contact with hydrazine to allow reaction, the OSH emulsifier which forms is an excellent emulsifier for hydrazine with a range of hydrocarbons. The OSH emulsifier preparation was studied and the emulsifier was partially characterized.

(a.) Preparation (U)

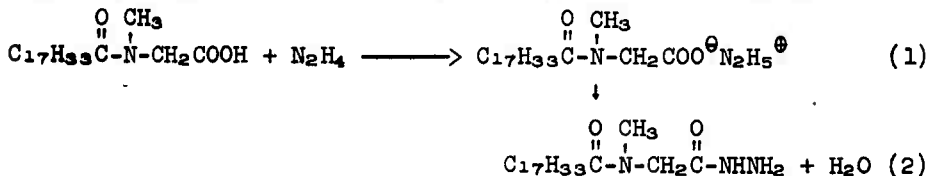
(C) The oleyl sarcosine is reacted with an excess of N_2H_4 as a solvent, preferably with 10 or more parts by weight of N_2H_4 to one part of oleyl sarcosine. The preferred amounts are 55 parts N_2H_4 to one part oleyl sarcosine, to which decane can then be added directly after the reaction to form the emulsion. The reaction and all handling of chemicals are under a dry, inert atmosphere such as nitrogen or argon. The N_2H_4 solution of the OSH emulsifier is considerably more viscous when the reaction is completed than the original solution of reactants.

(U) The rate at which the OSH emulsifier is formed depends on the temperature at which the reactants are held. At ambient temperature, the emulsifier is formed in 7 to 10 days, but at 55°C 18 hours is a sufficient reaction time. At 80°C the emulsifier is formed in about 5.5 hours. The favored reaction conditions are 18 hours at 55°C because of reproducibility.

(b.) Attempts to Characterize (U)

(C) The OSH emulsifier was isolated from the N₂H₄ solution as, a colorless waxy solid, which would emulsify the appropriate percentages of N₂H₄ and decane to a W/O emulsion identical to emulsions prepared with original N₂H₄ solutions of the OSH emulsifier. The wax was analyzed by various means, but the results were inconclusive.

(U) Hydrazine and oleyl sarcosine would be expected to react in two steps: (1) an immediate acid-base reaction to form an ionic hydrazinium salt, followed by (2) the slower conversion to the hydrazide with the elimination of a molecule of water.



(U) The observed time and temperature dependence in the OSH emulsifier preparation is consistent with Equations (1) and (2). However, elemental analysis of the wax is somewhat ambiguous (see Table IX), since the empirical formula C₂₁H₄₃N₃O₃ can represent both the hydrazinium salt and the hydrated hydrazide. The wax that was analyzed dried with difficulty and very possibly water could have been retained, even after several days under vacuum at ambient temperature. Infrared, nuclear magnetic resonance and mass spectrometry did not completely identify the OSH emulsifier.

Table IX

(U) Elemental Analysis of OSH Emulsifier

<u>Element</u>	<u>Calculated for C₂₁H₄₃N₃O₃, %</u>	<u>Found</u>	
		<u>By Combustion, %</u>	<u>By Neutron Activation, %</u>
C	65.41	65.2	--
H	11.24	11.2	--
N	10.90	10.5	13.0 ± 0.4
O	<u>12.45</u>	<u>12.7</u>	12.9 ± 0.6
	100.00	99.6	

(2.) Homogeneous Hydrazine/n-Decane Emulsions (U)

(U) To prepare a homogeneous W/O emulsion of N_2H_4 and decane with the OSH emulsifier, decane (2.5-6.0% by weight) is added to a N_2H_4 solution of the OSH emulsifier. The mixture emulsifies spontaneously to a thin O/W type emulsion, which then inverts to the thick, more stable W/O type emulsion after a few minutes of gentle shaking.

(U) The least amount of OSH emulsifier that could form the W/O N_2H_4 /decane emulsion was determined in a series of emulsion preparations. The concentration of OSH emulsifier was varied over the range of 0.2-3.3% in the study. The least amount of OSH emulsifier that produced a homogeneous emulsion was 0.42% and the emulsifier was stable at ambient temperature for four weeks before syneresis began. However, emulsions with 4% OSH emulsifier were stored for greater than 6 months at ambient temperature with no evidence of syneresis. Equivalent emulsions were heated to 55°C for three hours with no phase separation.

(3.) Heterogeneous Hydrazine/Hydrocarbon Emulsions (U)

(C) In this report, the term "heterogeneous emulsion" means an emulsion in which a solid phase is dispersed. Heterogeneous emulsions of N_2H_4 /decane with the OSH emulsifier can be prepared very simply by adding a solid metal or metal hydride to the homogeneous emulsion and mixing.

(C) The heterogeneous emulsions were optimized to obtain the best properties for the hydrazine/decane system with AlH_3 -1451 as the solid additive. Variations of the external hydrocarbon phase and the solid additive were explored.

(C) Ingredients of the heterogeneous emulsions can be combined in any order without significantly changing the physical properties of the finished emulsion. The ingredients can even be combined before the hydrazine-oleyl sarcosine reaction without detrimental effects. However, if AlH_3 -1451 is present during the reaction of the OSH emulsifier, the temperature should be kept at 60°C or lower.

(a.) With Decane (U)

(C) The physical properties of heterogeneous emulsions were studied for various concentrations of the OSH emulsifier and decane, the external phase. The AlH_3 -1451/ N_2H_4 ratio was maintained at approximately 40:60.

(U) Long-term physical integrity of the emulsions decreases at very low concentrations of emulsifier and external phase. As would be expected, the amount of emulsifier and external phase can be reduced to a point below which an emulsion cannot be formed. The lower limits that can produce an emulsion appear to be 0.2-0.3% OSH emulsifier and 0.7-1.0% decane. Samples with 0.5-1.0% OSH emulsifier were observed at ambient temperature for more than 6 months with no evident change.

(U) The yield stress of heterogeneous OSH emulsions varies inversely with emulsifier and external phase concentrations. As illustrated by the data presented in Figure 2, if the amount of external phase is increased from the lower workable limit for emulsion stability, the yield stress decreases from approximately 2000 dynes/cm.² to a range of 700-800 dynes/cm.² for concentrations of emulsifier above 0.4%. The highly stressed state of the emulsion at low emulsifier and external phase concentrations apparently restricts the movement of emulsion droplets and increases the stress required to cause flow. With more external phase, the stress within the emulsion is relieved slightly and the yield stress decreases.

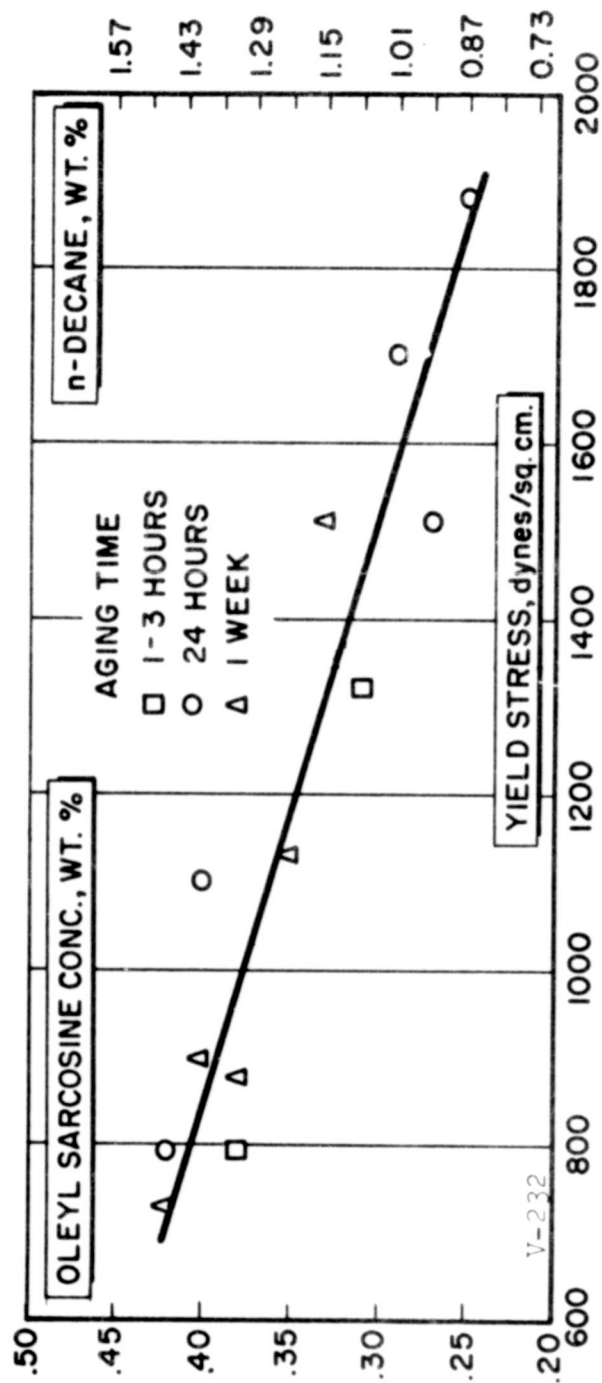
(C) The percentage of decane in heterogeneous N₂H₄ emulsions with OSH emulsifier was varied and all other components were held constant. The emulsions showed a decrease in yield stress with increased amounts of decane. The emulsions contained AlH₃-1451/N₂H₄ in a 40:60 ratio, 0.5% OSH emulsifier and decane in the range of 0.5-3.0% based on the total mixture. Initial formation of the emulsion required the most agitation for the lowest percentage of decane. The heterogeneous emulsions were also stiffest with the lowest percentages of decane, as shown by the yield stress values in Table X and Figure 3. The storage stability during more than eight weeks was good with all the emulsions, but was best with the greater amounts of decane. Adhesiveness increased with increased amounts of decane.

Table X

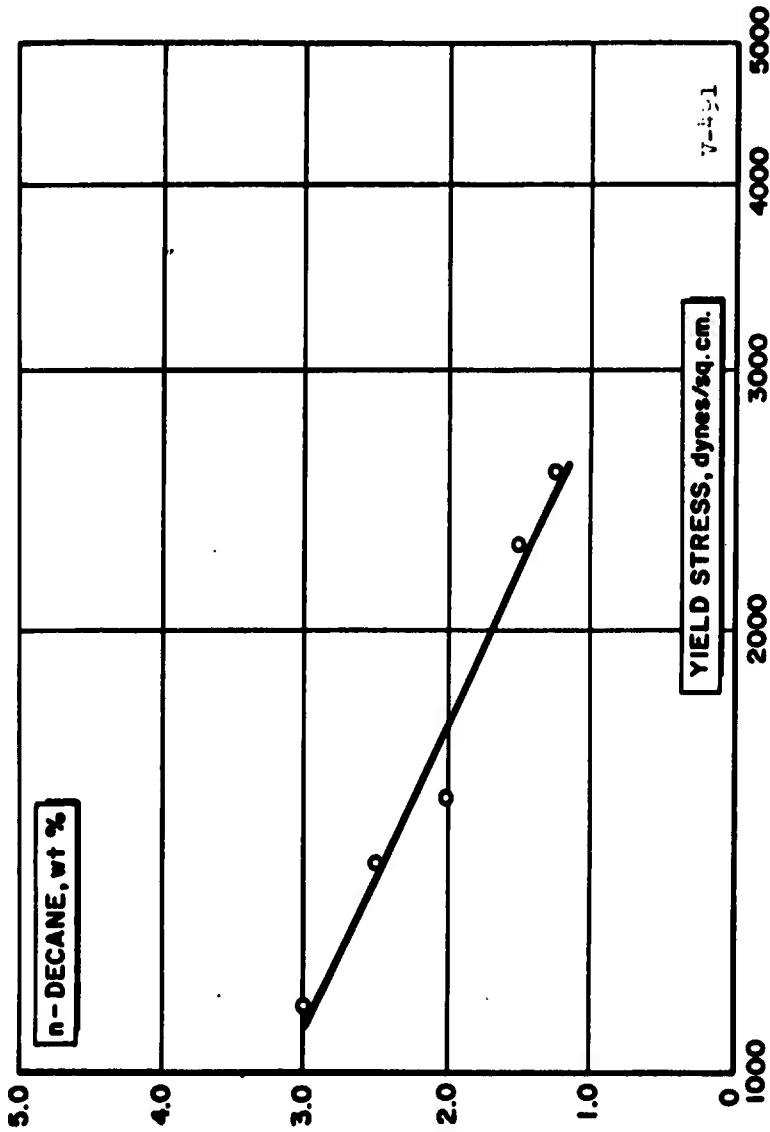
Amount of Decane vs Yield Stress in Heterogeneous
Hydrazine Emulsions with OSH Emulsifier (U)

<u>n-Decane</u> <u>%</u>	<u>Yield Stress,</u> <u>dynes/cm.²</u>
0.50	>2500
0.75	>2500
1.00	>2500
1.25	2560
1.50	2285
2.0	1540
2.5	1390
3.0	1110

(C) As a result of these studies the system that was chosen as optimum contained 0.5% OSH emulsifier, 1.75% decane and the balance of ingredients were AlH₃-1451/N₂H₄ in a 40:60 ratio.



(U) Fig. 2 - Effect of External Phase and Emulsifier Content On Yield Stress in Heterogeneous OSH Emulsions as Determined with a Microcapillary Rheometer



(U) Fig. 3 - Effect of External Phase Concentration on the Yield Stress of Heterogeneous Emulsions with 0.5% OSH Emulsifier

(C) Since the physical properties of emulsions varied when different lots of AlH_3 -1451 were formulated in the emulsions, a heterogeneous emulsion was prepared with small size AlH_3 -1451 crystals to determine the effect of crystal size on physical properties. A sample of 10-20 μ hydride was used instead of the usual 80-150 μ material. The emulsion contained 1.75% n-decane, 0.5% OSH emulsifier and the usual 40:60 ratio of AlH_3 -1451/ N_2H_4 . The yield stress of the emulsion was considerably higher (>2375 dynes/cm.²) than for a standard emulsion of the same composition with 80-150 μ crystals. The emulsion was slightly more cohesive than the standard emulsion, but not cohesive enough to overcome the adhesiveness of the emulsion systems.

(b.) With Other Hydrocarbons (U)

(C) Jet fuel was used in place of n-decane as the external phase in a heterogeneous emulsion which contained AlH_3 -1451/ N_2H_4 in a 40:60 ratio, 0.6% OSH emulsifier and 2.15% jet fuel. The translucent W/O emulsion formed easily, and was very stiff. The yield stress (2250 dynes/cm.²) was considerably greater than an emulsion of similar composition with n-decane (~800 dynes/cm.²). The yield stress did not change significantly during two weeks storage at ambient temperature, and storage stability appeared to be good. Probably higher concentrations of external phase in emulsions made with jet fuel would lower the yield stress to values equivalent to the emulsions with decane.

(U) In other external phase variations, a Number 1 fuel oil and benzene were the external phase for heterogeneous emulsions of N_2H_4 with the OSH emulsifier. The fuel oil formed a stable emulsion but contained contaminants that were incompatible with the N_2H_4 . The emulsion gassed excessively upon standing. Benzene formed a very unstable emulsion that broke shortly after mixing. The conclusion was drawn from these experiments that the external phase for stable emulsions of hydrazine with the OSH emulsifier can be aliphatic hydrocarbons in a boiling range from about 150-400°C, but that aromatics, such as benzene, are unsuitable.

(c.) With Aluminum Powder (U)

(U) Two heterogeneous N_2H_4 emulsions were prepared with aluminum powder for comparison with emulsions containing AlH_3 -1451. One emulsion contained OSH emulsifier and decane. The other contained H2246A emulsifier (sample from AFRPL) and jet fuel (2).

(C) The moderately thick, homogeneous emulsion with OSH emulsifier (1.5%) was prepared with N_2H_4 (55%) and decane (3.5%). Aluminum powder (Reyl-131 atomized, 40%) was added with moderate agitation. A smooth, very adhesive heterogeneous emulsion resulted, with a yield stress of 580 dynes/cm.² after twenty-four hours storage. The physical stability of the emulsion appeared to be good during four weeks of storage at ambient temperature.

(C) The extremely thick homogeneous emulsion with H4426A emulsifier (1.5%) was prepared with N_2H_4 (52%) and jet fuel (3.5%). The homogeneous emulsion was prepared by dissolving the emulsifier in the jet fuel and then adding the N_2H_4 in increments. The last half of the N_2H_4 entered the internal phase of the emulsion with difficulty. Aluminum powder (Reynolds 1-131 atomized 43%) was added and prolonged stirring was needed to produce a smooth, very thick, non-adhesive emulsion. During storage at ambient temperature for twenty-four hours the emulsion became thin and adhesive, which could have been caused by a reaction between the emulsifier and N_2H_4 . The yield stress of 570 dynes/cm.² after twenty-four hours of storage was nearly identical to the emulsion with OSH emulsifier and decane. The physical stability of both emulsions appeared to be equivalent during four weeks of storage.

(d) Evaluation Tests (U)

(U) During the screening and development of emulsions, promising candidates were evaluated by most of the tests described in Section III.A.1.b. that were used for gels. In most of the tests, emulsions with the OSH emulsifier compared very favorably to the candidate gels. However, three properties eliminated emulsions from further consideration.

(i) Cohesion (U)

(U) The stable heterogeneous emulsions adhered tenaciously to glass and metal surfaces. Emulsions appeared cohesive but non-adhesive only when syneresis had released N_2H_4 which could then wet surfaces and prevent adhesion. With the emulsions that were studied, cohesion could be gained only at the expense of emulsion stability.

(ii) Sensitivity to Atmosphere (U)

(U) Brief exposure to air was detrimental to heterogeneous emulsions with the OSH emulsifier. The mixtures gassed at a greater rate after contact with air, possibly because of water pickup.

(iii) Sensitivity to Temperature Cycling (U)

(U) Variation from ambient temperature (about 25°C) severely alters the physical integrity of heterogeneous OSH emulsions. The emulsions undergo extensive syneresis if cycled from freezing (below 10°C) to ambient temperature. An emulsion was held at 55°C for 8 hours before syneresis was observed. However, the elevated temperature apparently coalesced the emulsion droplets, because hydrazine exuded from the emulsion when it was allowed to stand for several days at ambient temperature.

(U) Since stable emulsions were consistently adhesive and also severely limited in usable temperature range, they were eliminated from further consideration as a candidate system.

B. STABILITY STUDIES (U)

(C) The chemical stability of the AlH_3 -1451/ N_2H_4 system and the individual components were studied in order to achieve the over-all stability requirements of less than 0.5 percent decomposition per year (calculated as mole percent hydrogen evolved from AlH_3 -1451) when the propellant is stored at 77°F. The investigation of the mutual compatibility of system components led to a treatment procedure for AlH_3 -1451 which greatly enhances its neat stability and compatibility in propellant systems that contain small amounts of water.

1. Preliminary Surveillance of Components and Mixtures (U)

(C) Stability problems of the individual components and their mixtures were investigated to provide a better understanding of the cause and magnitude of gas generation in AlH_3 -1451 systems. Water content of the hydrazine, type of AlH_3 -1451, surface treatment of the AlH_3 -1451 and thickening agents were studied. Results showed an initial gassing phenomenon, not caused by ordinary decomposition of the AlH_3 -1451, followed by long term stability in which either the initiation or propagation of the auto-catalytic decomposition of AlH_3 -1451 is partially blocked.

(C) Both the initial gas evolution and the long-term stability of the AlH_3 -1451/ N_2H_4 formulations are related to the water content of the N_2H_4 and surface conditions of the hydride.

(C) Initial gas generation of AlH_3 -1451/ N_2H_4 samples (with 0.1 to 0.8% H_2O in the N_2H_4) at 60°C is directly related to the water content. Samples of AlH_3 -1451 which have fresh surfaces, i.e. not oxidized or hydrolyzed, gas excessively when formulated in the wet N_2H_4 ; whereas with surface hydrolyzed hydride the initial gassing is reduced. A long term stabilization, which is not characteristic of experience with neat AlH_3 -1451, is also related to the water content in the hydrazine. AlH_3 -1451/ N_2H_4 mixtures which contain 0.3 - 0.8% water have better long-term stability than mixtures which contain 0.1% water. Of the various types of hydride studied, Mg-doped material (approximately 1% magnesium incorporated in the AlH_3 -1451 crystal lattice) was superior.

(U) With the gelling and emulsifying agents present, the thickening systems evolved slightly more gas initially than without the agents, but the long-term stability with the agents present was even better than the unthickened mixtures. A small amount of water carried into the system by the agents most likely causes the increased initial gassing.

a. Procedures (U)(1.) Thermal Stability Analysis (U)

(U) Gas evolution and swelling rates were measured in two types of apparatus, the standard Taliani method (3) and the glass dilatometers that were recommended by AFRPL (4). The details of these two test methods can be found in Appendix C. The majority

of samples were tested at 60°C by the Talliani method to accelerate decomposition and allow data to be accumulated in a convenient length of time. Reference samples were also tested at 25°C (77°F.), 40°C and 48.9°C (120°F.) to provide a firmer correlation for extrapolation of the 60°C. accelerated stability test data to more meaningful 25°C projections.

(C) The Talliani results are presented by two different techniques. The standard method of representing the off-gassing of AlH_3 -1451 propellants, that has been used by The Dow Chemical Company and many people in the solid propellant industry, is in terms of percent decomposition of the AlH_3 -1451. This technique is based on the assumption that all off-gas observed is produced by the decomposition of the AlH_3 -1451. The second technique often used by liquid propulsion researchers represents the gas generation in terms of change in volume, or amount of swelling of the liquid or gelled sample. This technique accounts for all generated gas without regard to source. However, when presenting swelling rates of liquid or gels it is necessary to keep in mind the fact that the amount of swelling is dependent not only on the number of moles of gas evolved but also on the pressure and temperature of the system. Unless properly corrected to a standard pressure and temperature, the swelling rates of various samples may be difficult to correlate. In this work, all swelling rates are presented as corrected to 25°C and 1 atm. pressure regardless of the temperature and pressure of the experiment. The swelling rates are expressed as volume of gas (cc.) (corrected to 25°C and 1 atmos.) evolved per minute per pound of propellant containing 40% AlH_3 -1451.

(2.) Hydrazine Analysis (U)

(C) The as-received N_2H_4 that was used throughout this work contained approximately 0.8% water and 0.5% aniline. Small amounts of N_2H_4 were distilled in a special apparatus for use in compatibility studies with AlH_3 -1451. The distilled N_2H_4 contained approximately 0.1% H_2O and 0.1% aniline.

(U) A gas chromatographic procedure was adapted for the analysis of water in N_2H_4 (5). A Beckman GC-2A chromatograph was equipped with a 1/4-inch, 9-foot stainless steel column packed with 10% Dowfax 9N9 on Teflon 6. With this column the elution of the peaks required about 15 seconds for ammonia, 2 minutes for water and 5 minutes for N_2H_4 . About 0.02% water in a synthetic hydrazine mixture was the lower limit that could be estimated by this method.

(U) Aniline content was analyzed by an ultraviolet spectrophotometric technique. The N_2H_4 content was measured by the "indirect iodate method" (6).

(3.) Aluminum Hydride-1451 Analysis (C)

(C) The relative amount of metallic aluminum formed by decomposition and its location with AlH_3 -1451 crystals was determined by a metallographic technique. The AlH_3 -1451 crystals were imbedded in a thermosetting resin which was then cured. The cured mass was cut and polished to expose a cross section of AlH_3 -1451 crystals. The cross section of the crystals was then photographed at 500 X magnification. Metallic aluminum was detected as bright reflective areas on a darker field of AlH_3 -1451.

(C) The C, H, N, Mg, Cl, and Li content of AlH_3 -1451 samples was analyzed by standard elemental techniques. These analyses helped to determine the effect of various treatments on the composition of AlH_3 -1451 samples.

(b.) Components (U)

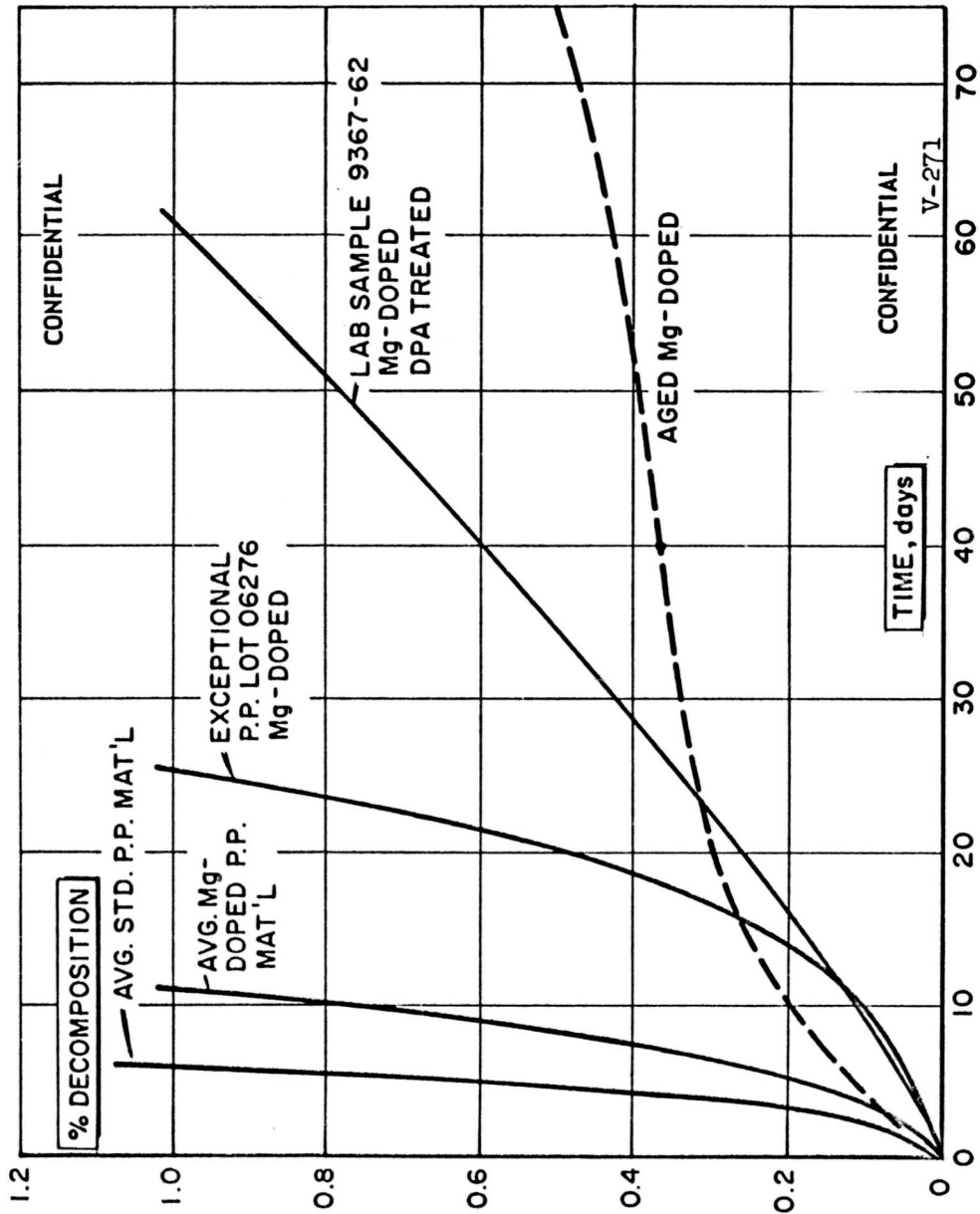
(C) In considering the chemical stability and compatibility of the components making up the heterogeneous AlH_3 -1451/ N_2H_4 system, the components and combinations thereof were studied separately and in combination. Two of the components of the system are known to decompose slowly under ambient conditions. The decomposition products include N_2 , H_2 and NH_3 . The decomposition of the AlH_3 -1451 is believed to proceed auto-catalytically with the formation of H_2 and Al.

(1.) Hydrazine (U)

(U) The decomposition of N_2H_4 , both neat and containing aluminum powder, has been studied by many investigators (10,11). The decomposition reaction generally results in the formation of N_2 and NH_3 . The decomposition rates of gelled metallized N_2H_4 propellants usually decrease with time, presumably due to poisoning of a decomposition catalyst. In our studies it was determined that the amount of decomposition of the N_2H_4 was negligible compared to the gas produced by the AlH_3 -1451. Therefore, the decomposition of N_2H_4 was not extensively studied. The purity of the N_2H_4 , however, was found to have great effect on the off-gas rates in combination with AlH_3 -1451 and this will be discussed in detail later.

(2.) Aluminum Hydride-1451 (C)

(C) The mechanism of decomposition of AlH_3 -1451 has been less extensively studied, but relative decomposition rates have been measured for many samples. Figure 4 presents the results of some 60°C stability tests of various types of AlH_3 -1451. The more stable samples represent current laboratory produced material, whereas the least stable material is comparable to 1965 pilot plant product.



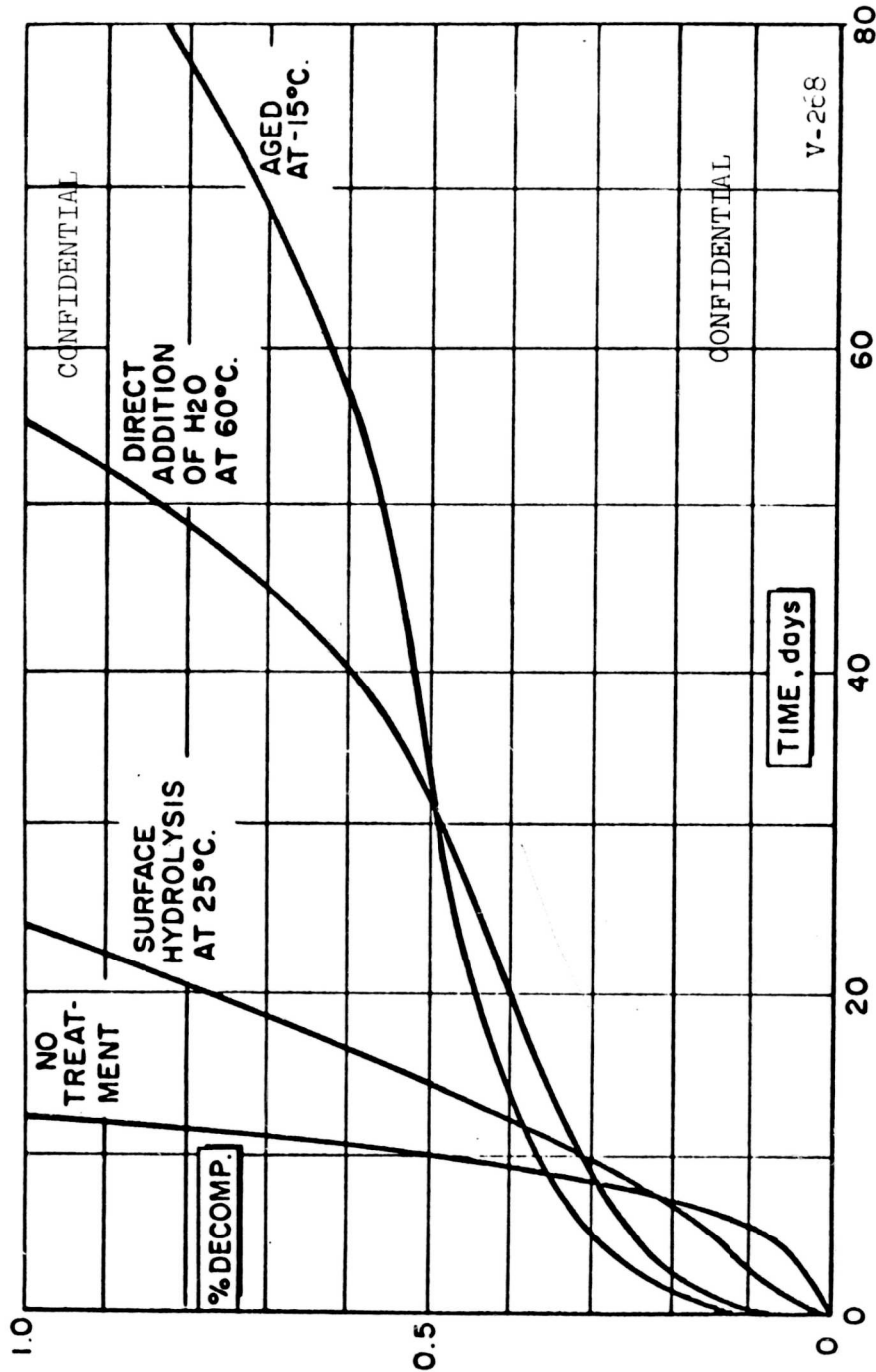
(U) Fig. 4 - Improvements in the 60°C. Stability of Aluminum Hydride-1451

(C) The improvement in the stability of AlH_3 -1451 has been accomplished through improved crystallization, Mg doping, and surface treatments. The improved crystallization is a result of modifications in the process in which AlH_3 -1451 in the 1451 crystal phase has been recovered from an ether solution of AlH_3 etherate. With these improvements, the AlH_3 -1451 crystal size has been increased to approximately 100 μ with at least a twofold improvement in stability, over the earlier fine powder (5 μ) AlH_3 -1451.

(C) The incorporation of 1 to 2 wt. % magnesium in the crystal has been found to be an effective stabilizer for AlH_3 -1451. The doping is accomplished by adding soluble $\text{LiMg}(\text{AlH}_4)_3$ to the AlH_3 /ether reaction solution. The Mg-doped hydride has been found to have slightly expanded crystal lattice dimensions, compared to normal hydride, as determined by X-ray diffraction studies. The lattice dimensions, along with very accurate density measurements, indicate that magnesium is present substitutionally in the hydride crystal rather than interstitially. The Mg-doped hydride generally exhibits approximately a twofold improvement in stability compared to normal (non-doped) AlH_3 -1451.

(C) Surface treatment of AlH_3 -1451 crystals has been used to improve the stability and compatibility of the hydride. Washing the hydride with acrylonitrile was one of the most extensively used treatments. The benefits obtained from these washing treatments are now believed to be at least partially due to a surface hydrolysis of the hydride which occurred because of trace quantities of water present in the treatment liquor. Other methods of surface hydrolysis of the hydride have been investigated and often a large stabilization of the hydride is observed. Figure 5 shows the type of decomposition curves obtained with hydride hydrolyzed in wet benzene at 25°C and by the direct addition of water. The "aged" sample is also believed to be surface hydrolyzed, caused by contamination of the sample with oxygen or water during storage. Although the surface hydrolyzed samples have better long-term stability, they have a characteristic initial gassing which would prevent their use in heterogeneous liquid systems. The elimination of this initial gassing and with the maintenance of the long-term stability was the subject of a great deal of research which will be discussed under pretreatment below.

(C) AlH_3 -1451 has been observed to be more stable in certain propellants than when neat. Studies to elucidate this phenomenon led to the discovery that symmetrical diethyldiphenylurea, designated ethyl centralite, does stabilize the hydride. Screening of additional potential stabilizers led to the discovery that diphenylacetylene (DPA) was a very effective stabilizer. AlH_3 -1451 is now routinely washed with an ether solution of DPA, leaving approximately 1 wt. % DPA on the surface of the hydride. Certain laboratory batches of Mg-doped AlH_3 -1451 treated with DPA required more than 50 days to reach 1% decomposition at 60°C, which is better than a twofold improvement over the untreated Mg-doped hydride.



(c) Fig. 5 - Effect of Water on the Decomposition of Aluminum Hydride-1451 at 60°C.

(3) Aluminum Hydride/Hydrazine Formulations (U)

(C) The gas generation characteristics of AlH_3 -1451/ N_2H_4 formulations have been critically studied. It would be predicted from stability data of AlH_3 -1451 and N_2H_4 that the gas generation from AlH_3 -1451 would far exceed the gas generation of N_2H_4 , and this led to a more detailed examination of the hydride and factors which affected its stability.

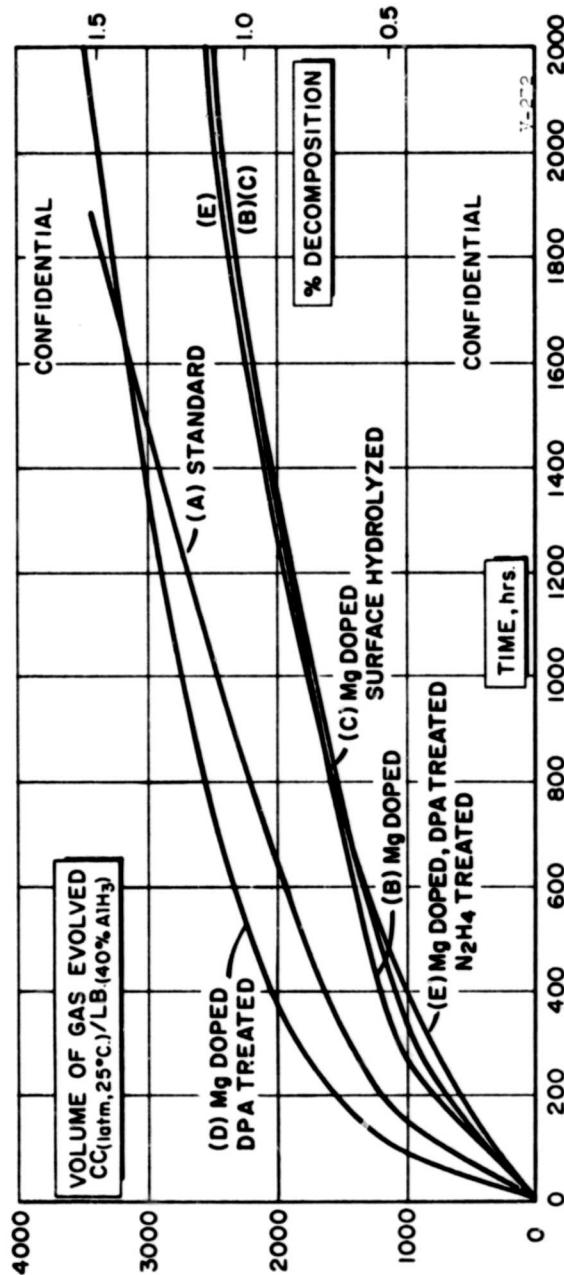
(a) Type of Aluminum Hydride-1451 (U)

(C) Four types of AlH_3 -1451 were formulated as 40 wt. % mixtures in as-received N_2H_4 . The types of hydride included: (A) standard, (B) Mg-doped, (C) Mg-doped, surface hydrolyzed, and (D) Mg-doped, DPA treated AlH_3 -1451. The results of accelerated stability testing at 60°C of these formulations are shown in Figure 6. In all cases a rapid evolution of gas was first observed, followed by a decreasing gas generation rate. The samples differed primarily in the amount of "initial gassing" and were similar in the gas generation rates observed after 1200 and 2200 hours, as shown in Table XI. The results of these four samples indicate all of the Mg-doped samples are more stable than the standard hydride. The value of the DPA treatment of AlH_3 -1451 which is to be formulated with hydrazine is questionable, since it is believed the DPA dissolves from the hydride in hydrazine. A fifth sample (E) in this series, which is shown in Figure 6 and Table XI, contains Mg-doped, DPA treated hydride which had been treated for 15 days in as-received hydrazine at 60°C before being tested in hydrazine. Significant reduction of the amount of gas evolved from the formulation the first 300 hours was observed. This approach to reducing the gassing of the AlH_3 -1451/ N_2H_4 formulations has been further evaluated as discussed later in this Section.

Table XI

(C) Gas Generation Rates of AlH_3 -1451/Hydrazine Formulations
Containing As-Received Hydrazine at 60°C .

<u>Type of AlH_3-1451</u>	<u>Gas Generation Rate, cc./ (lb. min.)</u>	
	<u>@1200 Hrs.</u>	<u>@2200 Hrs.</u>
Standard Lot No. 02055 (A)	0.019	--
Mg-doped Lot No. QX-020 (B)	0.011	0.0078
Mg + Surface Hydrolyzed Lot No. QX-020 (C)	0.011	0.0076
Mg + DPA Lot No. 09236 (D)	0.014	0.0073
Mg + DPA Lot No. 09236 + N_2H_4 Treated (E)	0.013	0.0068



(C) Fig. 6 - Gas Evolution vs. Time for Various Types of AlH₃-1451 in As-Received N₂H₄ at 60°C.

(b.) Water Content of Hydrazine (C)

(C) The relationship of the water content of the hydrazine to the amount of initial gassing of the $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ formulations was investigated. Figure 7 shows the effect of varying the water content from 0.1 to 0.8%. The $\text{AlH}_3\text{-1451}$ used in this study was Mg-doped and DPA treated; however, similar results have been obtained with standard hydride. As shown in Figure 7, an increase in water content results in an increase in initial gassing of the formulation. However, an increase in water content also results in an increase in the induction period (length of time before accelerated decomposition begins) of the hydride decomposition. Apparently the initial gas, which has been identified as hydrogen, is not a product of thermal decomposition of the hydride, but rather a product of a reaction between the hydride and the hydrazine or water in the hydrazine.

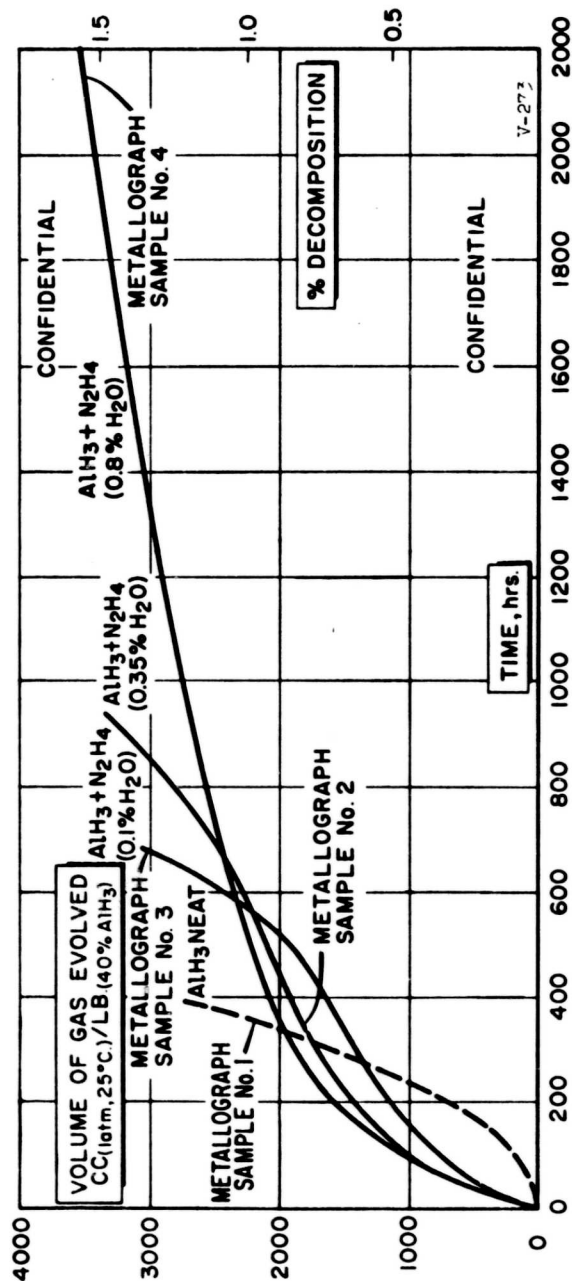
(C) Using the metallographic technique, analysis of hydride recovered from the accelerated stability test further substantiates that the initial gassing is not produced by typical decomposition of the hydride. The metallographic photographs are shown in Figure 8 and the conditions under which the samples were taken are shown in Figure 7. Metallographic Sample Number 1 shows the noticeable presence of aluminum (appears as white spots) in a sample of hydride which had decomposed 1.0% after 15 days neat at 60°C . Metallographic Sample Number 2, which had been on test an equal amount of time, 15 days in hydrazine at 60°C , and had evolved nearly as much gas, shows no detectable aluminum present.

(C) Similarly, in Sample Number 4, even after 95 days at 60°C in as-received hydrazine (0.8% H_2O), very little aluminum is detected. Sample Number 3, taken just at the end of the induction period for a sample of hydride in distilled hydrazine (0.1% H_2O), shows the beginning of aluminum formation.

(C) It can be concluded from these studies that the initial gassing of the $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ formulations is related to the water content of the hydrazine. The initial gas is not generated by typical thermal decomposition of the hydride but is a product of a $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ (or water) reaction. The stability of the $\text{AlH}_3\text{-1451}$ in the as-received hydrazine is phenomenal, with very little decomposition of the hydride after more than 100 days at 60°C , which would correspond to approximately 3 years at 25°C . The long-term stability of $\text{AlH}_3\text{-1451}$ in hydrazine (0.8% H_2O) is very much better than the stability of neat hydride.

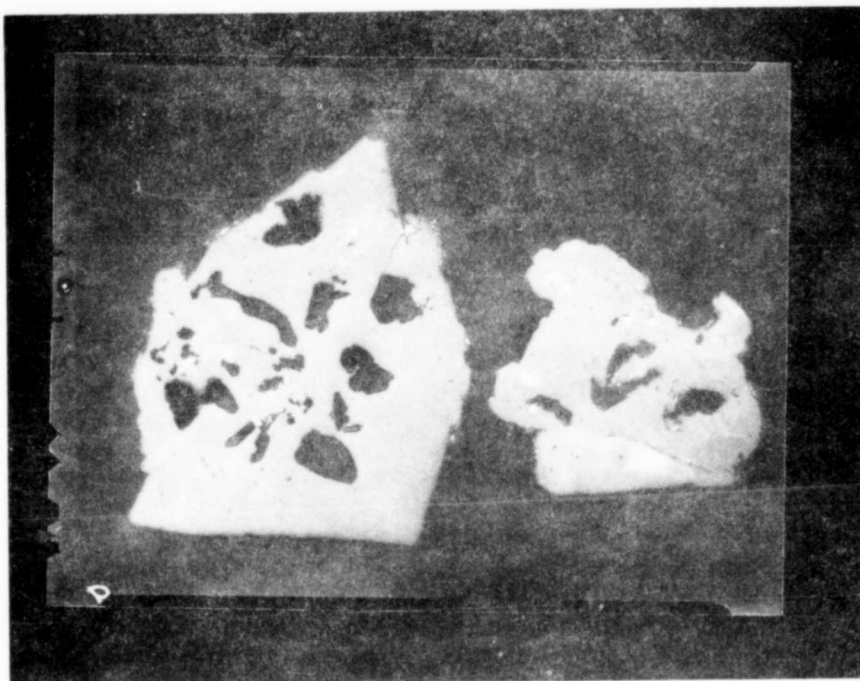
(c.) Gel and Emulsion Systems (U)

(C) The gas generation characteristics of four gelled and one emulsified $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ heterogeneous propellant systems have been studied at 60°C . The results of these samples are shown in Figure 9 along with an ungelled $\text{AlH}_3\text{-1451/N}_2\text{H}_4$ reference formulation. In all cases the gelled or emulsified systems evolve more initial gas than the reference. The increased initial gassing may be caused by water carried into the systems by the gelling

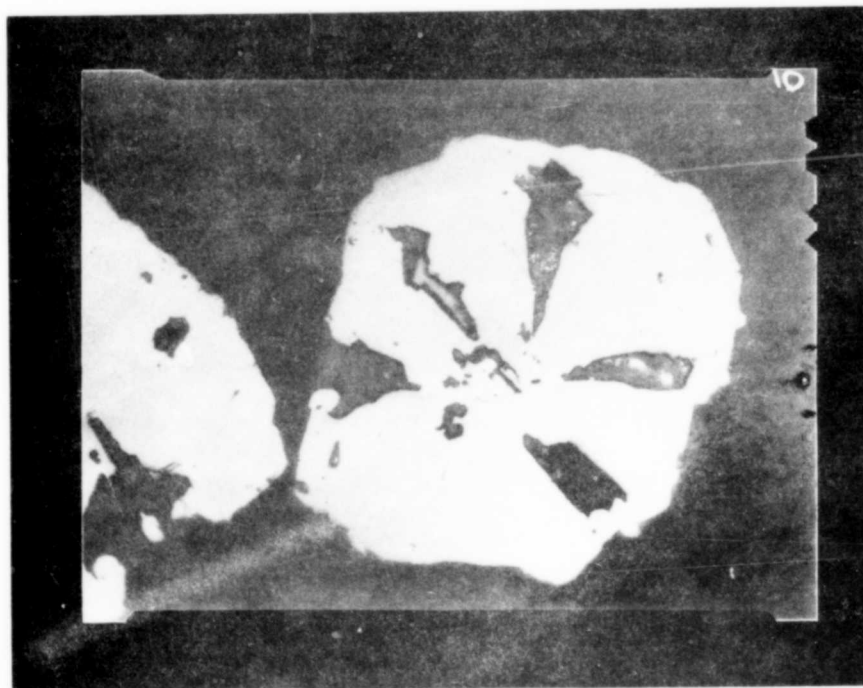


(C) Fig. 7 - Affect of Water Concentration in Hydrazine on the Decomposition of Aluminum Hydride-1451 at 60°C. in Formulations

1. Neat after 15 days

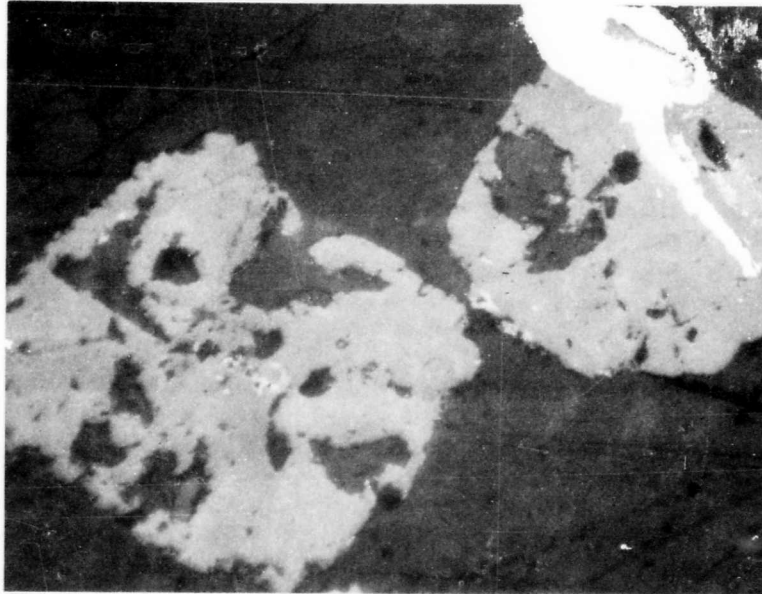


2. In Hydrazine (0.35% H₂O) after 15 days

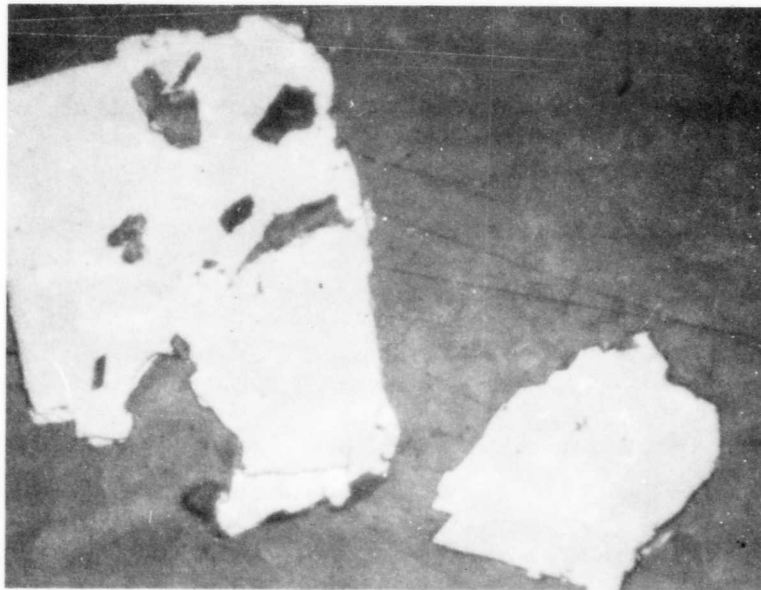


(C) Fig. 8 - Metallograph Studies of Mg-Doped, DPA-Treated Aluminum Hydride-1⁴⁵1, Texas Lot 09236, Recovered from 60°C. Taliani (500X Magnification)

3. In Hydrazine (0.1% H₂O) after 27 days

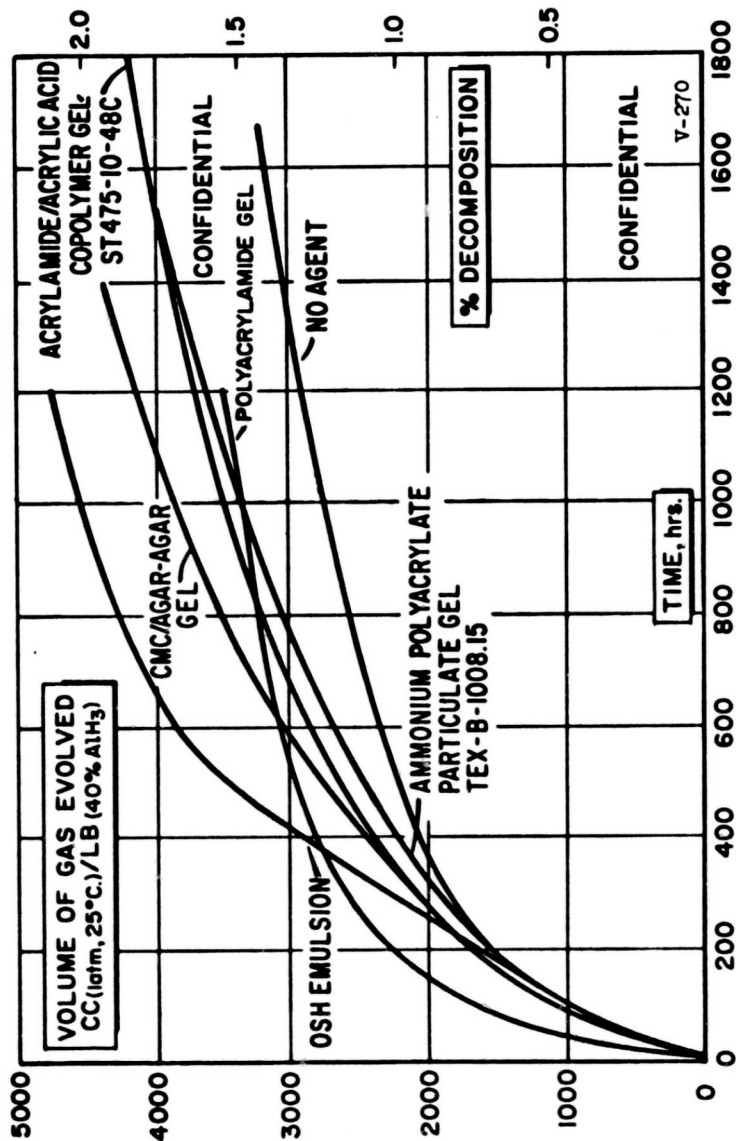


4. In Hydrazine (0.8% H₂O) after 95 days



(C) Fig. 8 (Contd.)

P122



(C) Fig. 9 - Gas Generation vs. Time of Gel and Emulsion Formulations Containing As-Received Hydrazine + Lot 09236 (Mg + DPA) Aluminum Hydride-1451 at 60°C.

or emulsifying agents. All of the systems show a gas generation rate decreasing with time. The gas generation rates of the various systems after 1200 hours are listed in Table XII for comparison. The difference in long-term generation rates of the various systems appears to be relatively insignificant.

Table XII

Gas Generation Rates of Aluminum Hydride/Hydrazine Formulations Containing As-Received Hydrazine at 60°C.* (C)

<u>Gelling or Emulsifying Agent</u>	<u>Gas Generation Rate @1200 Hrs., cc./lb. min.</u>
--	1.4×10^{-2}
OSH emulsion	4.5×10^{-2}
CMC/agar-agar gel	2.5×10^{-2}
Acrylamide-acrylic acid copolymer gel	1.7×10^{-2}
Ammonium polyacrylate gel	1.9×10^{-2}
Polyacrylamide gel	0.8×10^{-2}

* Lot No. 09236: Mg-doped, DPA-treated AlH_3 -1451

2. Pretreatment of Aluminum Hydride-1451 (U)

(C) It was recognized early in the program that the initial gas evolution in AlH_3 -1451/ N_2H_4 formulations would be detrimental to long term storage of the heterogeneous propellant. To reduce this initial gas evolution and gain the benefits of long term stability, pretreatment studies were conducted. One of the most effective AlH_3 -1451 pretreatment procedures was with hydrazine (0.8% H_2O) at 60°C. for >100 days. The initial gas evolution was greatly reduced, but the treatment time was inconveniently long. Pretreatment parameters were studied in as-received hydrazine to determine more precisely the factors that influence the reduction of initial gas evolution. Several treatment liquids were given precursory evaluations to find a system which would reduce the initial gas evolution as effectively as hydrazine, but in a much shorter time period. The most effective pretreatment medium was found to be n-butylamine. In the discussion which follows, all tests were with a hydride:treatment liquid ratio of 40:60, unless otherwise noted.

a. Studies of Treatment Parameters in Hydrazine (U)

(C) Several treatment parameters were varied in the hydrazine pretreatment procedure to determine their effect on the amount of initial gassing that occurs when the hydride is reformulated with hydrazine. Pretreatments with temperatures greater than 60°C, a greater proportion of hydrazine in the pretreatment mixture, and water content of hydrazine >0.8% were tried.

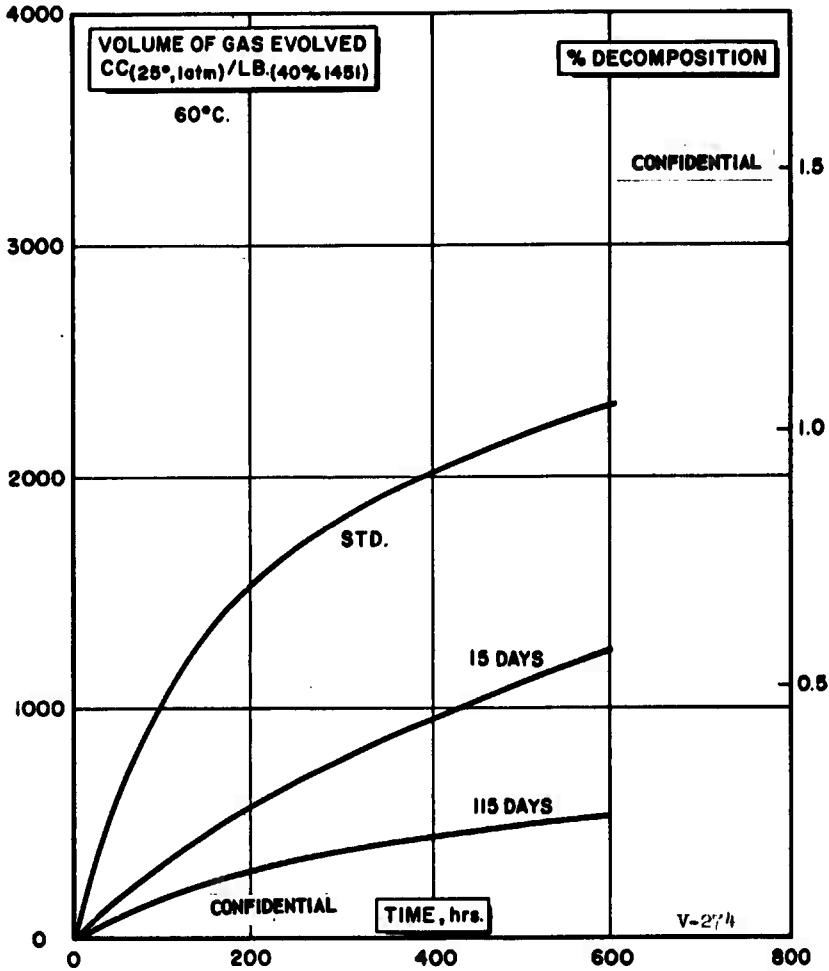
(1.) Treatment Temperature (U)

(C) The reduction of initial gassing was accomplished by a 15 and 115 day pretreatment of the hydride in as-received hydrazine at 60°C as illustrated in Figure 10. The hydride was dried before being reformulated in the hydrazine, then tested at 60°C in a modified Taliani apparatus.

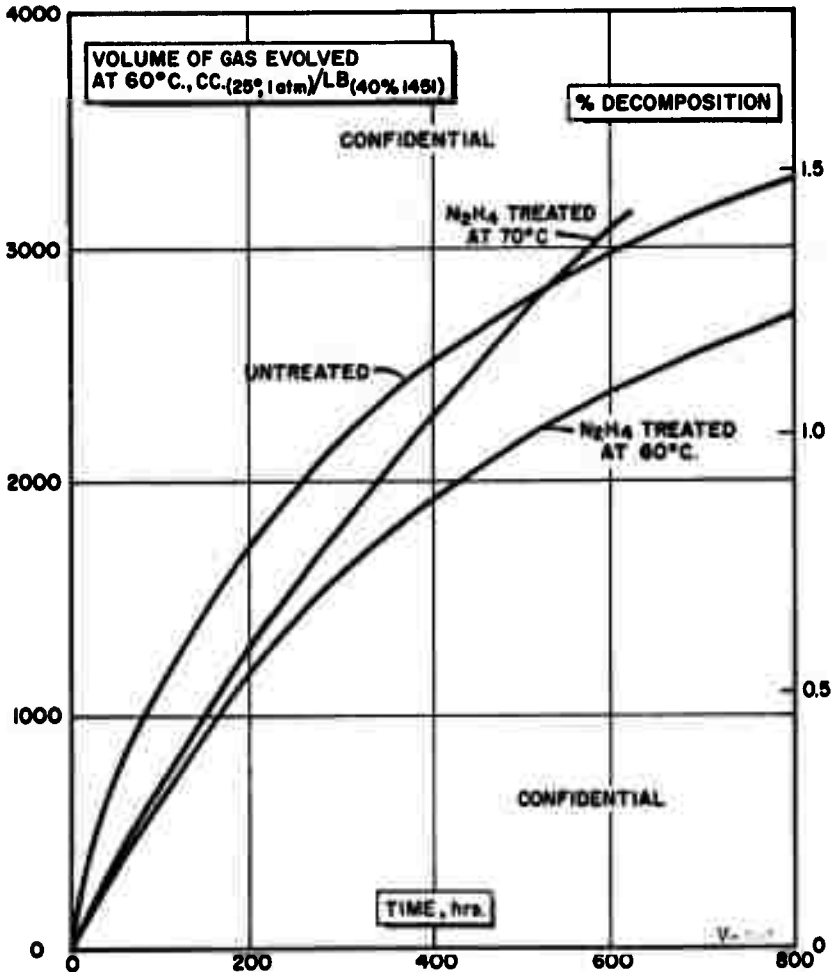
(C) When AlH₃-1451 was allowed to stand in contact with as-received hydrazine at 70°C for 6 days, recovered, dried, and reformulated with as-received hydrazine and placed in a 60°C Taliani apparatus, it was shown that the higher pretreatment temperature caused a reduction of initial gassing, as illustrated in Figure 11. Although this experiment was conducted for only 6 days, it was quite evident that the more elevated temperature will not speed up the process. In addition, the oxygen content of the sample treated at 70°C was 0.98%, as compared to 0.78% after the 60°C treatment. These results indicate that the pretreatments of AlH₃-1451 should be kept at approximately 60°C, since a higher and lower temperature have produced less effective stabilizations.

(2.) Water Content of Hydrazine (U)

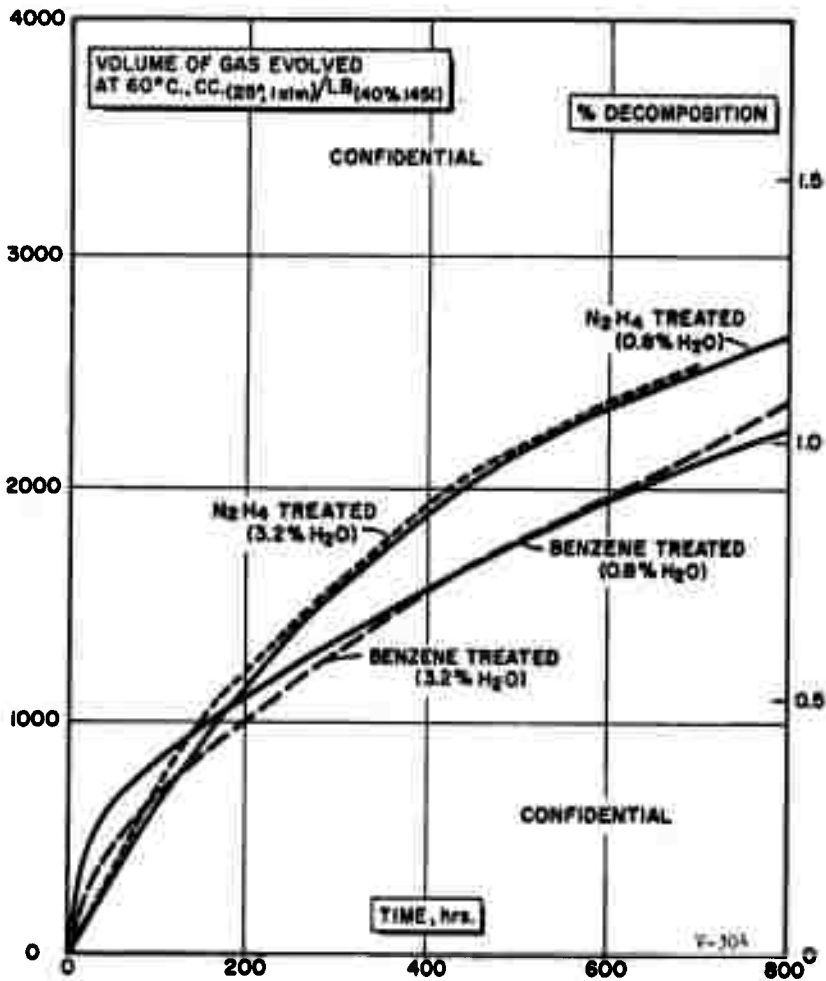
(U) The amount of water in hydrazine was shown to be proportional to the amount of initial gas evolution and to the degree of long term stabilization of AlH₃-1451/N₂H₄ formulations. This was shown by experimental data with hydrazine containing 0.1 - 0.8% water. The most effective concentration was found to be 0.8% water. To determine if a greater amount of water would decrease initial gassing in a shorter pretreatment time, hydrazine with 3.2% water was used in a 6 day pretreatment experiment. The treated sample was recovered from the hydrazine, dried and reformulated in as-received hydrazine. The sample was tested in the 60°C Taliani apparatus. The results (see Figure 12) indicate that there is no benefit in using increased concentrations of water. Also presented in Figure 12 is benzene pretreatment stability data. Pretreatment with benzene containing either 0.8% or 3.2% water produces approximately the same stability when the hydride is reformulated in as-received hydrazine. After benzene treatment with 0.8% water, the hydride contained 1.74% oxygen, and with 3.2% water the hydride contained 3.86% oxygen. On a long term basis, compatibility of the system after the benzene treatment appears to be slightly better than after the hydrazine treatment, but the excessive amount of hydrolysis shows benzene to be impractical.



(C) Fig. 10 - Effect of Pretreatment Time on the Gas Generation Rate of Aluminum Hydride-1451 in Hydrazine



(C) Fig. 11 - The Effect of Treatment Temperature on the Gas Generation of Aluminum Hydride-1451 (Lot 09236) in As-Received Hydrazine



(C) Fig. 12 - The Effect of Water Content in Pretreatment on Gas Generation of Aluminum Hydride-1451 (Lot 09236) in As-Received Hydrazine

(3.) Aluminum Hydride-1451/Hydrazine Ratio (C)

(C) A study was conducted to determine the effect of increasing the amount of hydrazine to AlH_3 -1451 in the total pretreatment mix. This effectively doubled the amount of water in contact with the hydride. The stability data presented in Figure 13 indicate a slightly better reduction in initial gas evolution with the increased amount of hydrazine. The amount of hydrolysis also was increased as indicated by the oxygen analysis. It was felt that the slight increase in stability did not warrant the added expense of doubling the amount of pretreatment hydrazine.

(4.) Other Treatment Liquids (U)

(C) In order to reduce both the time and the cost of pretreatment of AlH_3 -1451, a number of pretreatment liquids were investigated. The screening of these liquids consisted of a six-day, 60°C treatment of the hydride and the liquid, followed by recovery of the hydride, drying, and formulation with as-received hydrazine for stability testing on the Taliani apparatus. In all cases, the hydride/treatment liquid ratio was 40:60 on a weight basis.

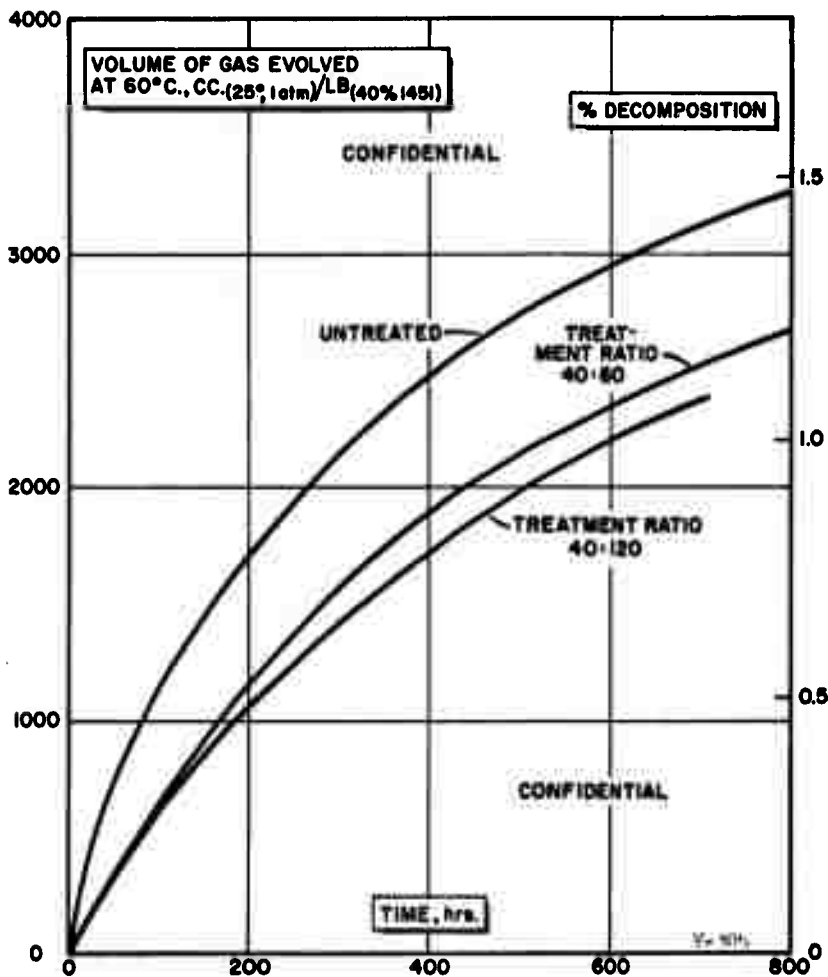
(C) A summary of the data collected in this effort is presented in Appendix B. Of the treatment liquids tested, n-butylamine and ethyl alcohol were shown to have the most promise of reducing initial gas evolution in less treatment time than hydrazine. This is shown in Figure 14. Tetrahydrofuran, n-propanol and ethyl acetate were not as effective. A six-day treatment with n-butylamine produced better stabilization than an 18-day treatment with hydrazine with only a moderate increase in the hydride oxygen content. The alcohol treatment was intermediate in effectiveness between six-day treatments with hydrazine and n-butylamine.

(C) The best overall results were obtained with n-butylamine and this pretreatment liquid was chosen for the scale-up effort and the preparation of the final heterogeneous propellant.

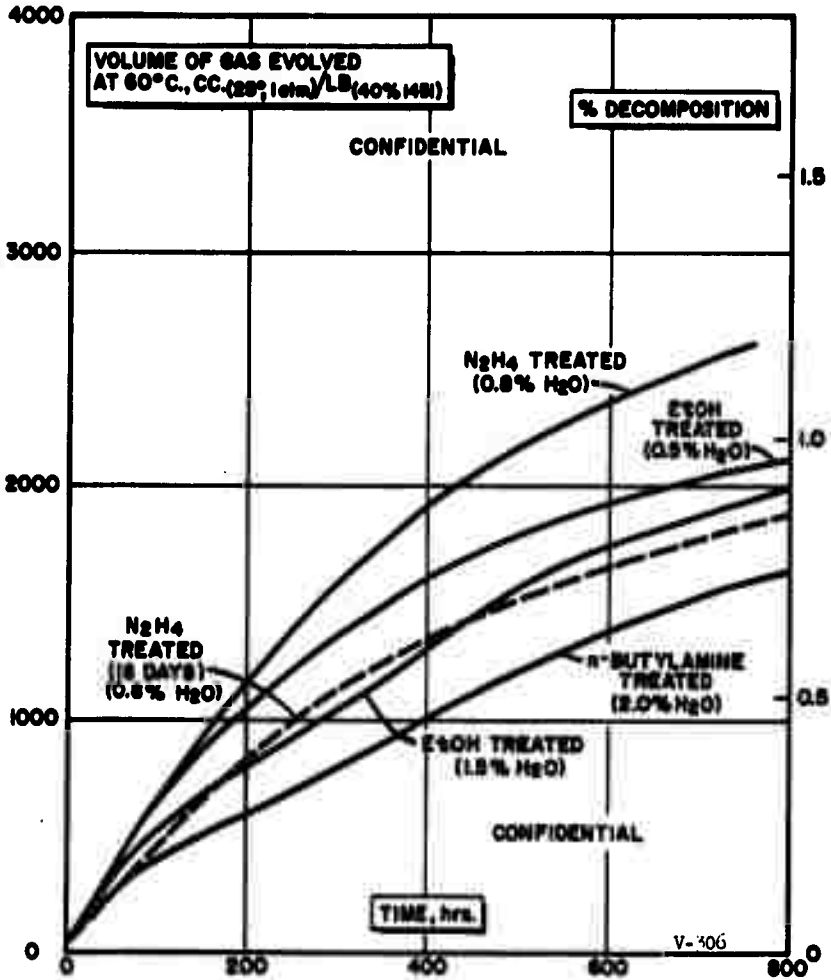
b. Pretreatment With n-Butylamine (U)

(C) Pretreatment with n-butylamine was chosen as the most effective means of stabilizing AlH_3 -1451 that is to be formulated with N_2H_4 . The recommended procedure for the pretreatment is as follows:

(C) The AlH_3 -1451 (2 parts by weight) is placed in a round-bottom flask. n-Butylamine (3 parts by weight) is added and the mixture, under an inert atmosphere, is heated to $60^\circ \pm 0.5^\circ\text{C}$ for 18 days. The n-butylamine was Fischer reagent grade, 98%, with 2% water. If 0.5 pounds or more of AlH_3 -1451 is being treated, gentle agitation is required to insure sufficient solid-liquid contact. A flask with 50% ullage should be used to allow for expansion during heating and gas evolution during the early portion of the heating.



(C) Fig. 13 - Effect of Aluminum Hydride/Hydrazine Ratio in Pretreatment on Gas Generation of Aluminum Hydride-1451 (Lot 09236) in As-Received Hydrazine



(C) Fig. 14 - Gas Generation of Six-Day Pretreated Aluminum Hydride-1451 (Lot 09236) in As-Received Hydrazine with Various Agents

(C) While the mixture is still warm, the liquid is decanted and the remaining solid washed with a fresh portion of n-butylamine, which is again decanted. The treated hydride is dried by vacuum at room temperature until condensate ceases to be collected in a dry ice trap in the vacuum line. Drying is continued at 40°C for 16 hours to insure that trace amounts of water are removed from the treated AlH₃-1451.

(C) The effectiveness of the treatment is evaluated by the Taliani test in combination with N₂H₄ as described in Appendix C.I. The stability of AlH₃-1451 in heterogeneous gels is discussed below.

c. One-Year Storage Data (U)

(C) The gas evolution rates of gelled propellants were tested at 77°F and 120°F to determine one-year storage stability. The propellants were tested by both the Taliani method and the glass dilatometer method (Appendix C). The total gas evolution during the one-year storage was within the requirement of less than equivalent to 0.5% decomposition of AlH₃ per year at 77°F.

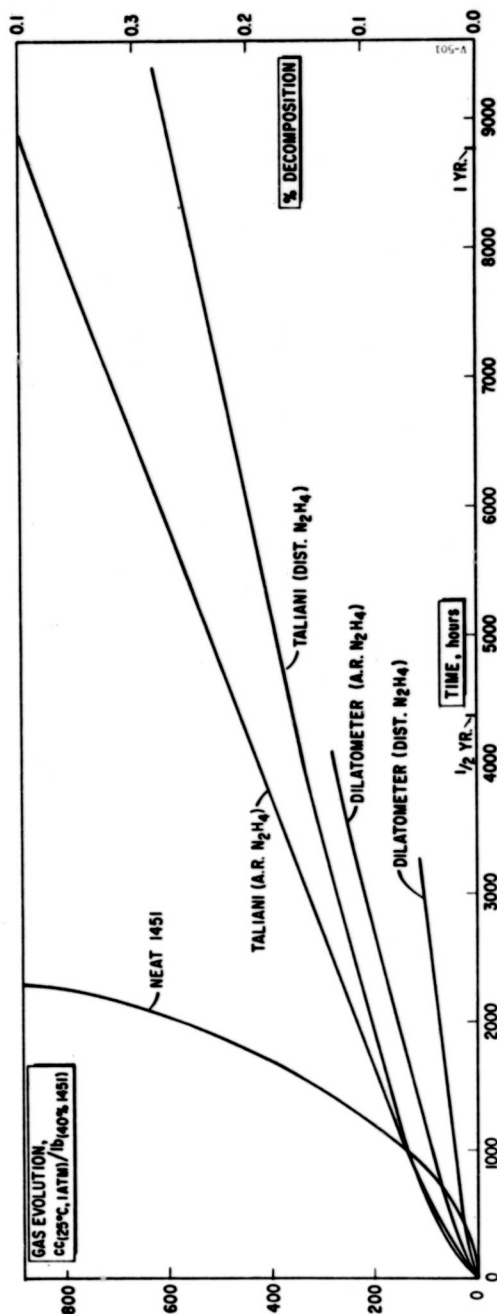
(1.) Gels at 77°F. (U)

(C) The gel formulation that was tested in all of the one-year stability work contained AlH₃-1451 (40 parts) that had been pretreated in n-butylamine and N₂H₄ (60 parts) gelled with 0.5% polyacrylamide gelling agent. Two types of N₂H₄ were used: as-received propellant grade which contained about 0.8% water, and laboratory distilled N₂H₄ which contained about 0.1% water. One-gram samples of gel were tested by the Taliani method at 77° and 120°F. One-hundred gram samples were tested in the glass dilatometers at 77°F only.

(U) The pressure rise of the samples by both test methods at 77°F are shown in Figure 15. The initial gassing phenomenon is evident, but minor, at 77°F. With time, the rate of gas evolution decreased as is shown in Table XIII. The sealed dilatometer test method appeared to be less severe than the Taliani method which is vented to atmospheric pressure at intervals. Possibly, the gas evolution was suppressed by the pressure build-up in the sealed dilatometers.

(U) The dilatometer tests were terminated before one complete year of testing. Since the dilatometers were not designed with sufficient ullage for gels with the swelling rate that was measured, the gel expanded into the capillary and blocked free movement of the mercury.

(C) The gels in the Taliani method were tested for one complete year. The total decomposition at the end of one year at 77°F was 874 cc./lb. or 0.395% for the gel containing as-received hydrazine and 590 cc./lb. or 0.2669% for the gel containing distilled hydrazine.



(C) Fig. 15 - Storage Stability of Heterogeneous Gels at 77°F.

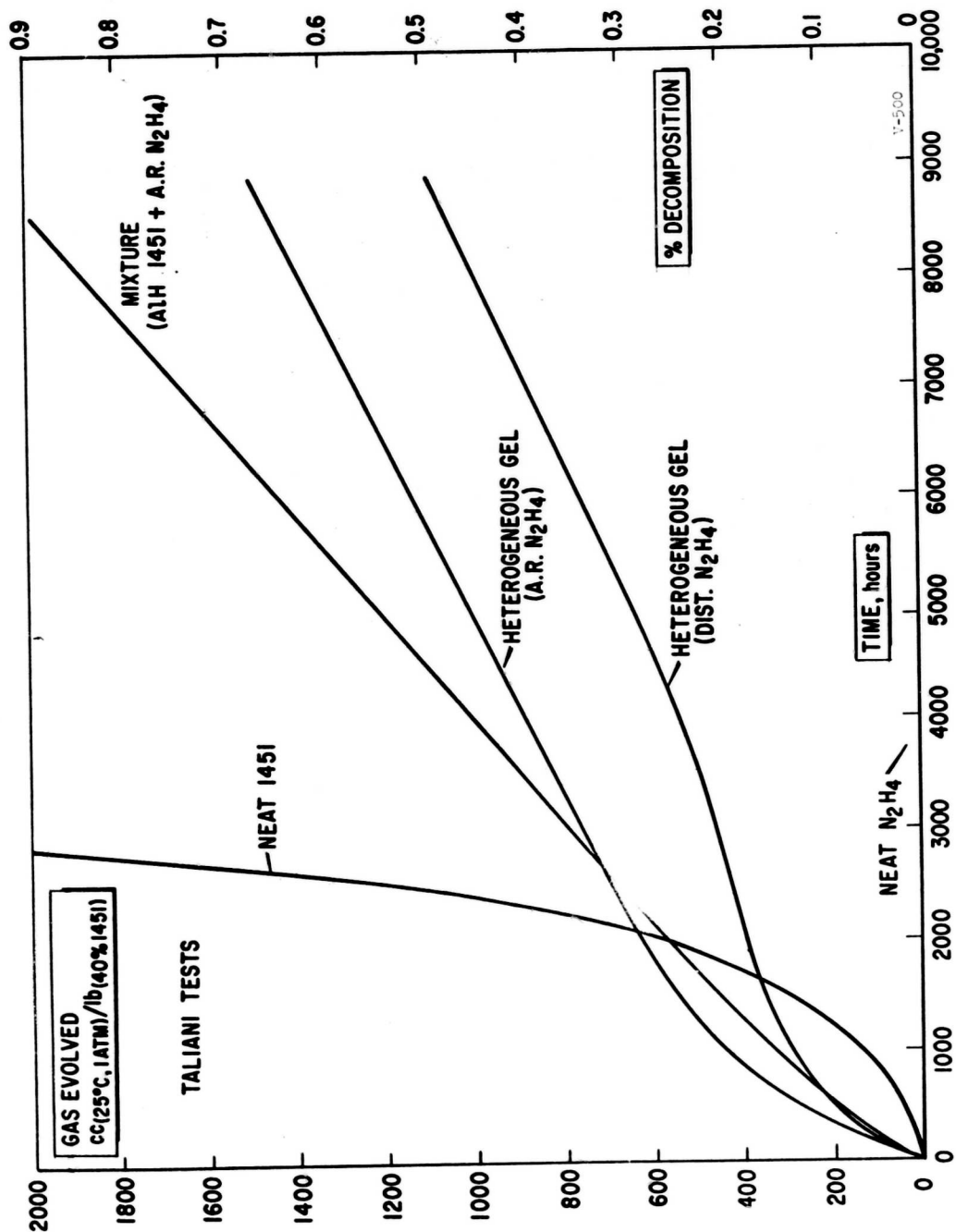
Table XIII

(C) One-Year Storage Stability Test at 77°F.

Time at 77°F., hrs.	Gassing Rate, cc./lb. min.			
	Taliani Method		Dilatometer Method	
	N ₂ H ₄ Type		N ₂ H ₄ Type	
	As-Received	Distilled	As-Received	Distilled
300	3.2×10^{-3}	--	1.0×10^{-3}	7.3×10^{-4}
1000	1.5×10^{-3}	1.3×10^{-3}	1.0×10^{-3}	5.0×10^{-4}
1800	1.6×10^{-3}	1.2×10^{-3}	1.1×10^{-3}	5.6×10^{-4}
2300	1.7×10^{-3}	1.1×10^{-3}	8.1×10^{-4}	4.8×10^{-4}
3000	1.6×10^{-3}	1.1×10^{-3}	8.8×10^{-4}	5.0×10^{-4}
3800	1.3×10^{-3}	9.2×10^{-4}	9.9×10^{-4}	--
4200	1.3×10^{-3}	9.2×10^{-4}	--	--
5800	1.6×10^{-3}	8.9×10^{-4}	--	--
7000	1.7×10^{-3}	8.9×10^{-4}	--	--
8760	1.5×10^{-3}	8.9×10^{-4}	--	--

(2) Gels and Components at 120°F. (U)

(C) Heterogeneous gels (identical to the gels tested at 77°F) and the individual components were tested for one-year storage stability at 120°F by the Taliani method (See Figure 16). The gas evolution data are presented in Table XIV. Neat N₂H₄ evolved an insignificant amount of gas compared to the tests containing AlH₃-1451. The neat AlH₃-1451 followed the usual autocatalytic type of accelerating decomposition and the test was terminated at 1% decomposition (approximately 3000 hours). The mixture of AlH₃-1451 and distilled N₂H₄ gassed less initially, but was less stable at extended times than the heterogeneous gel with propellant grade N₂H₄ (0.8% water). The heterogeneous gel with distilled N₂H₄ (0.1% water) had low initial gas evolution and excellent long-term stability for the first six months of testing. However, the gas evolution rate with the distilled N₂H₄ began to accelerate after six months, which confirmed suspicions that a minimum amount of water greater than 0.1% was needed for extended stability of heterogeneous gels of AlH₃-1451 and N₂H₄.



(C) Fig. 16 - Storage Stability of Heterogeneous Gels at 120°F.

Table XIV

(C) One-Year Storage Stability Test at 120°F.

<u>Time at 120°F.</u> <u>hours</u>	<u>Gassing Rate, cc./lb. min.</u>			
	<u>AlH₃-1451</u>	<u>AlH₃-1451/ N₂H₄</u>	<u>AlH₃-1451/ N₂H₄/Agent</u>	<u>AlH₃-1451/ Dist. N₂H₄/ Agent</u>
600	2.0×10^{-3}	4.2×10^{-3}	5.2×10^{-3}	4.1×10^{-3}
1300	5.8×10^{-3}	5.1×10^{-3}	4.7×10^{-3}	9.2×10^{-4}
2000	1.0×10^{-2}	2.9×10^{-3}	1.8×10^{-3}	1.6×10^{-3}
2700	--	3.4×10^{-3}	2.0×10^{-3}	6.4×10^{-4}
3400	--	3.4×10^{-3}	2.1×10^{-3}	8.15×10^{-4}
4200	--	3.5×10^{-3}	2.1×10^{-3}	1.6×10^{-3}
5400	--	3.5×10^{-3}	2.1×10^{-3}	1.8×10^{-3}
7000	--	3.7×10^{-3}	2.1×10^{-3}	2.0×10^{-3}
8760	--	3.7×10^{-3}	2.1×10^{-3}	2.1×10^{-3}

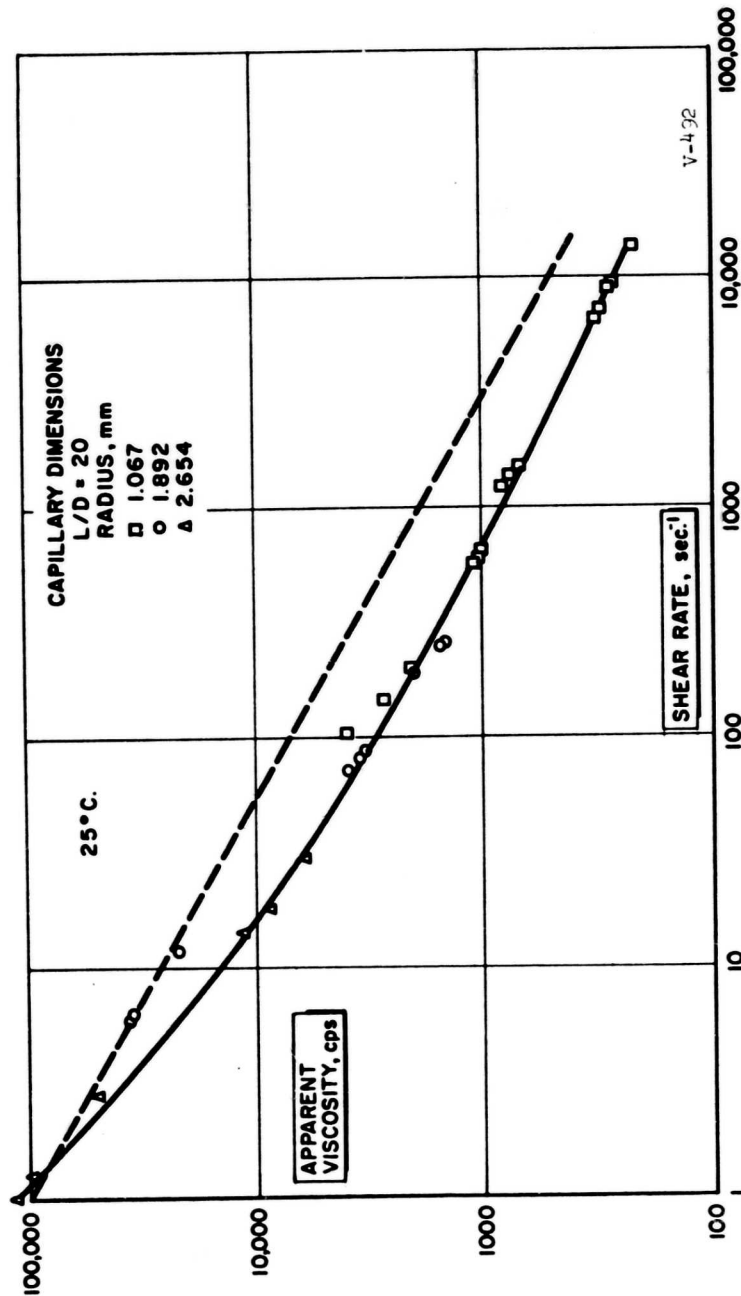
C. SYSTEM CHARACTERIZATION (U)

(C) After a system was chosen for further development in Phase I of this work, i.e. AlH₃-1451/N₂H₄ (40:60) gelled with a polyacrylamide gelling agent (0.5-0.6%), the physical and chemical properties of the heterogeneous gel were characterized to supply engineering data on the propellant system. In the following sections the flow curve, density vs. temperature, mechanical stability, minimum usable temperature, and thermal stability from room temperature to boiling of the gel are discussed

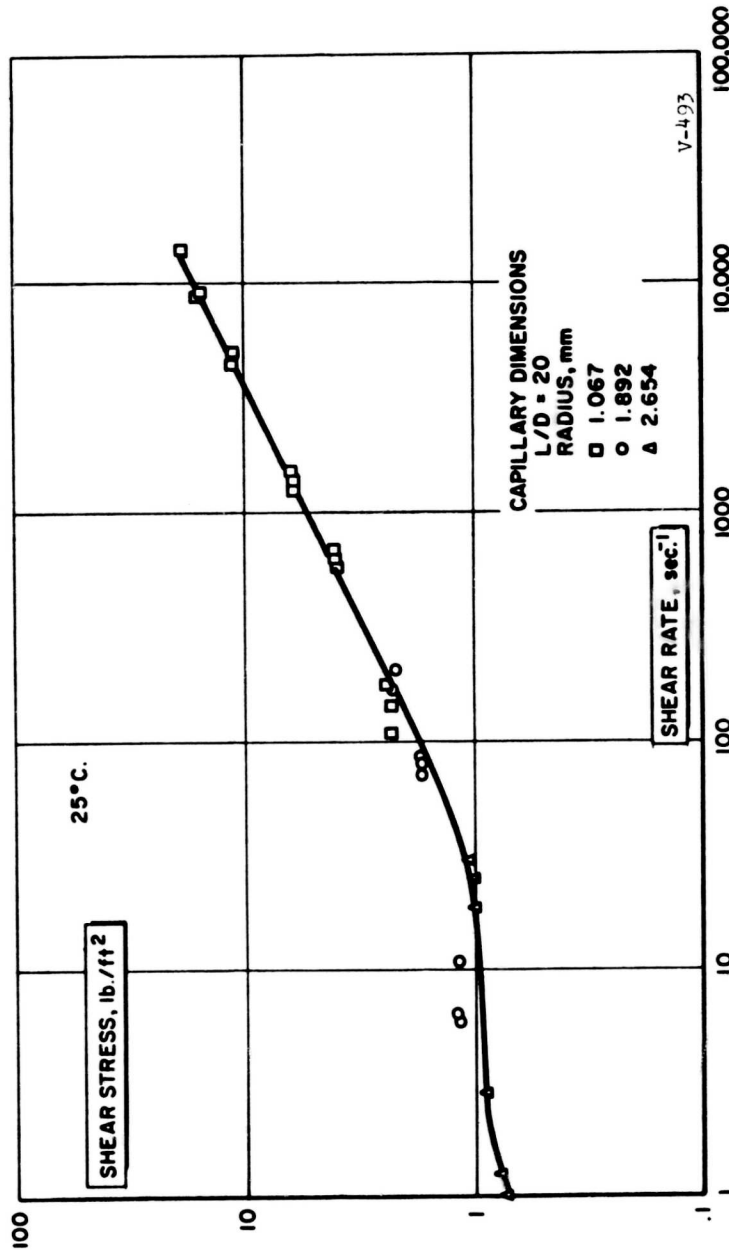
1. Flow Curve (U)

(U) The rheological properties of the thixotropic gelled propellant were studied with a capillary viscometer. The flow properties are presented graphically by plots of both apparent viscosity vs. shear rate (Figure 17) and the flow curve (Figure 18), i.e. shear stress ($DP/4L$, lb./ft.²) vs. shear rate ($32 Q/D^3$, sec.⁻¹).

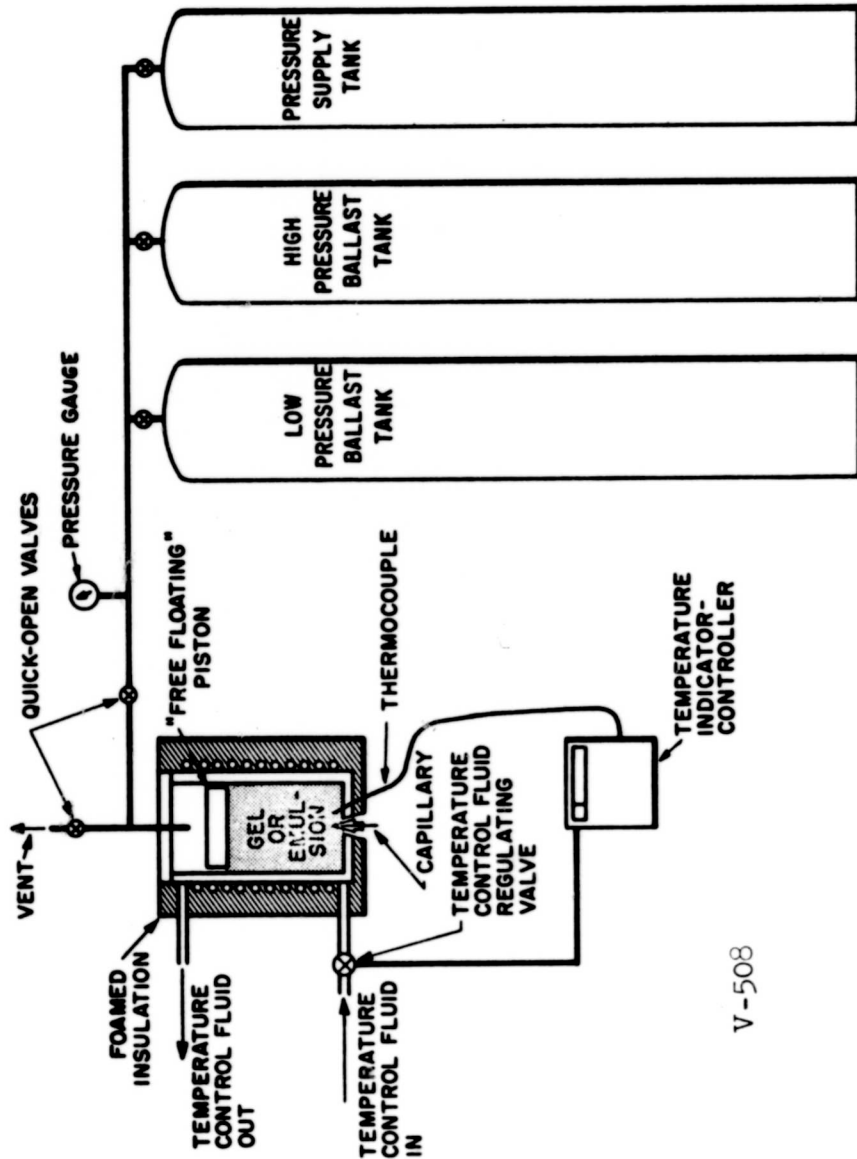
(U) A capillary viscometer was constructed to measure the flow properties of the gel. A diagram of the apparatus is shown in Figure 19. The viscometer is operated by nitrogen gas pressure which forces the gel through a capillary. Flow rates and shear rates in the viscometer are varied by regulating the nitrogen pressure and/or interchanging capillaries (diameters = 0.2133, 0.2784, and 0.531 cm.; L/D = 40).



(C) Fig. 17 - Apparent Viscosity vs. Shear Rate for the Heterogeneous Gel BHS 39-64
0.6% Agent, 5 Days After Preparation, with a
Yield Strength of 690 dynes/cm²



(c) Fig. 18 - Shear Stress vs. Shear Rate for the Heterogeneous Gel BHS 39-64



(U) Fig. 19 - Capillary Viscometer System

(U) The capillary viscometer system includes an automatic electric timer and automatic electrically operated valves. A schematic diagram of the apparatus is shown in Figure 20. The operating procedure for the viscometer follows.

(U) The viscometer is loaded with gel in a dry box and the closed unit is then connected to the pressure source. The ballast pressure is set at the desired value. An accurately weighed receptacle is placed in the receptacle holder. The holder is then moved in place as the handle is pushed (to the right, Figure 20). As the receptacle holder is moved, first relay Nr. 1 is opened which closes the vent line solenoid, then relay Nr. 2 is closed which opens the pressure line solenoid. At this point the capillary begins to discharge into the purge receptacle. As the handle is pushed further, simultaneously the weighed receptacle moves under the capillary and relay Nr. 3 is activated, which starts the electric timer. After the desired sample is collected, the handle is pulled back which stops the timer, closes the pressure line solenoid, and opens the vent line solenoid.

(C) Trial viscometer runs with standard oils and greases agreed with specified viscosities of the samples. A trial run with a Number 1 grease which contained 40% KCl (100 μ) to simulate a heterogeneous gel with AlH_3 -1451 was also run satisfactorily.

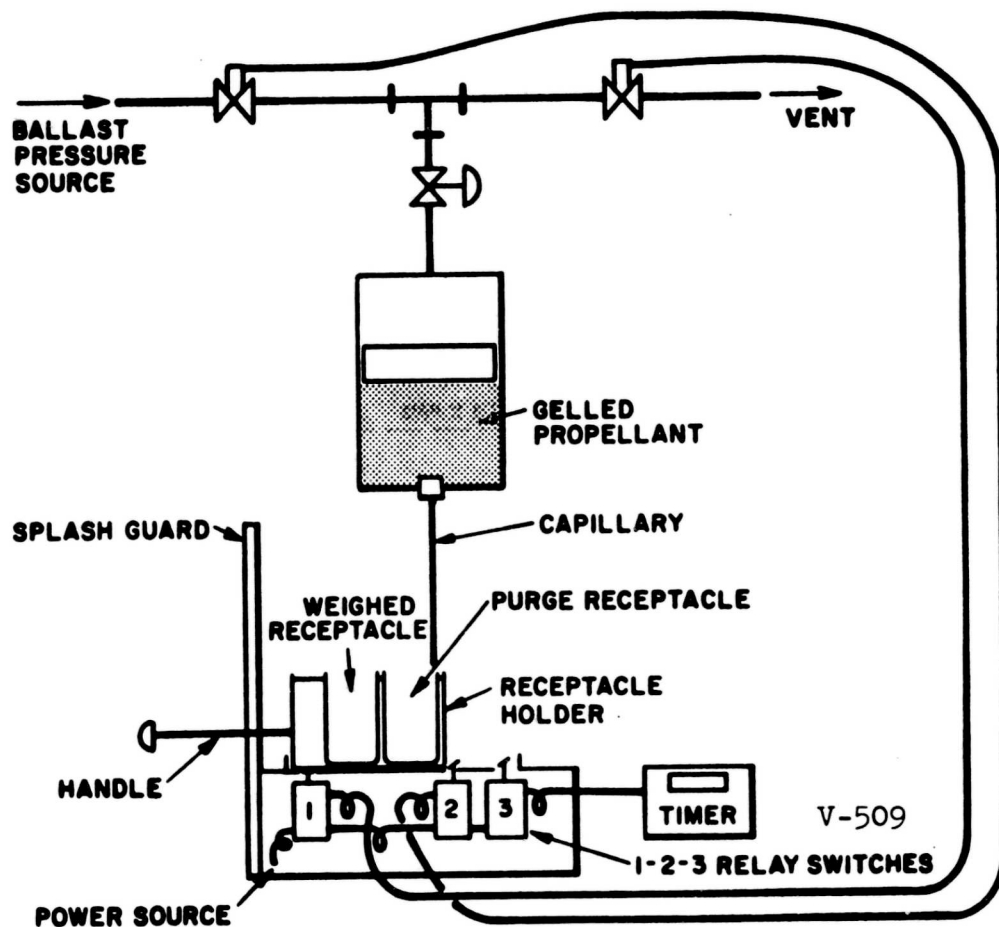
(C) During propellant development work, samples of AlH_3 -1451/ N_2H_4 (40:60) heterogeneous propellant were tested in the capillary viscometer as a screening device. The results obtained from these three gels and one emulsion are shown in Figure 21 along with the contract specification. Figure 21 demonstrates the shear thinning properties of these samples at high shear rates and shows them to be within the contract specification in that range.

(C) After the polyacrylamide gel was selected as the system of choice, the shear rate was extended to the lower range for that gel. As was seen in Figure 17, the apparent viscosity for the polyacrylamide gel is within contract specification, but approaches the limiting value at a shear rate of 1 sec^{-1} . At that shear rate, the shear stress is barely sufficient to keep the propellant flowing and the yield strength of the gel interferes with an accurate measurement in that range of shear stress and shear rate.

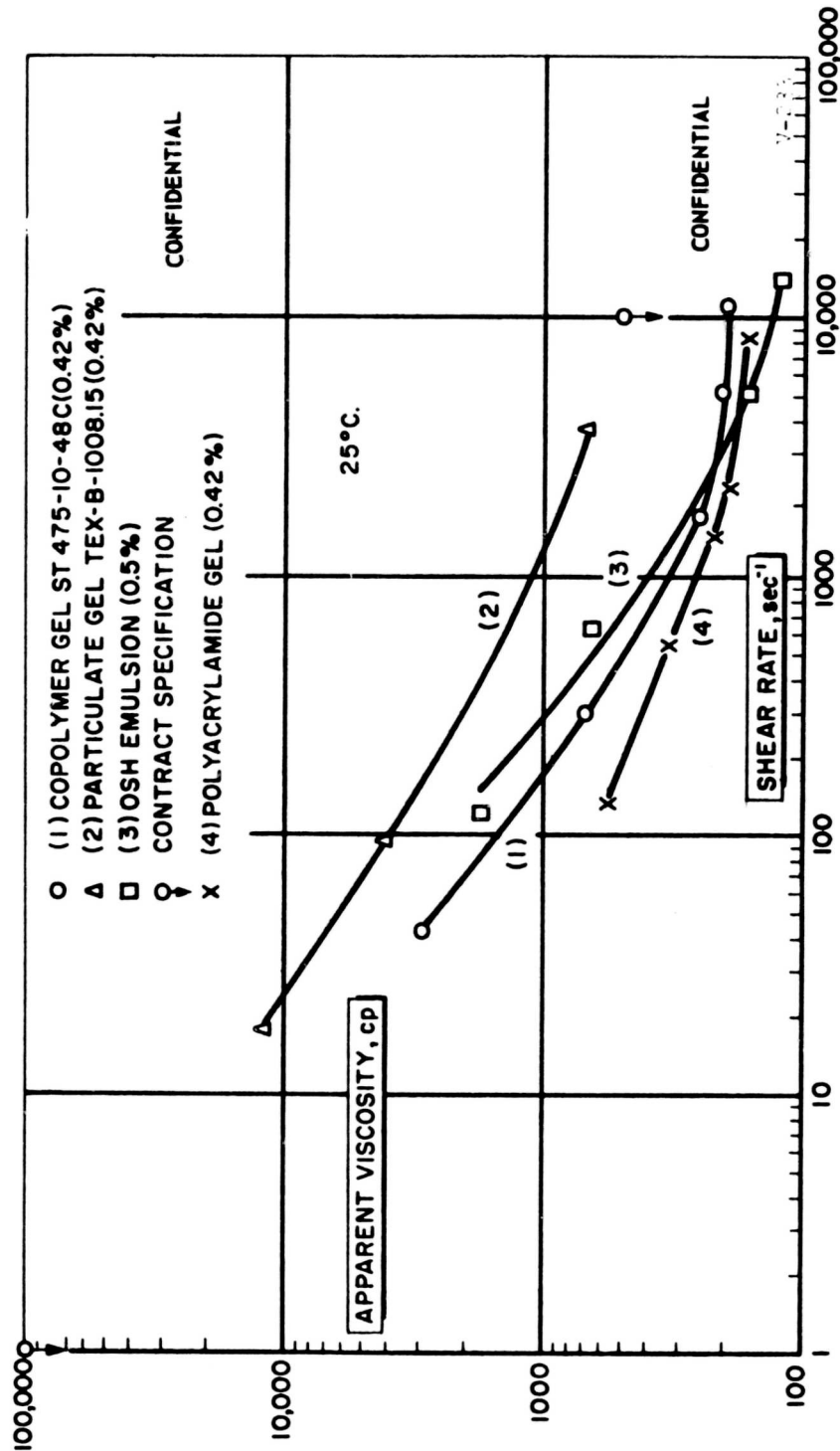
2. Density vs. Temperature (U)

(U) As part of the complete characterization of the polyacrylamide heterogeneous gel, the density was determined at 40°, 60°, 80°, and 100°F. The density measurement method with a pycnometer is listed in Appendix C. IV.

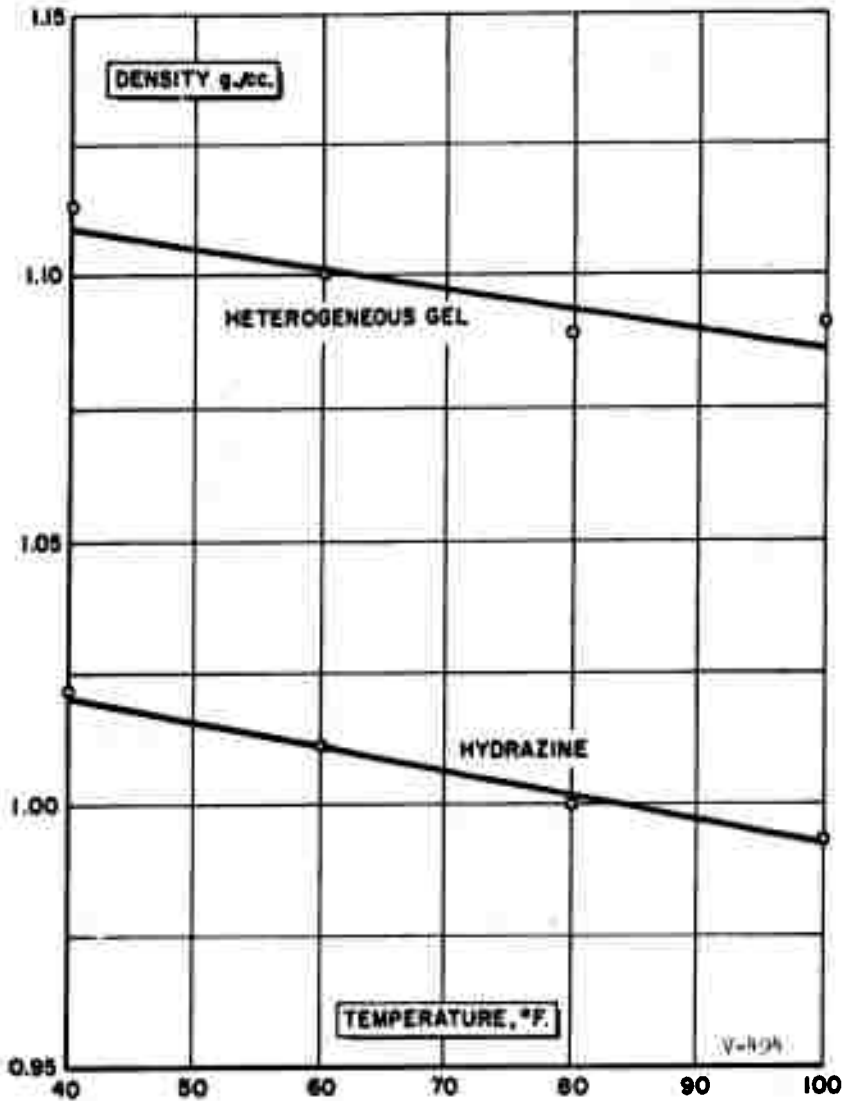
(U) The measured data on density vs. temperature are presented in Figure 22, with data on hydrazine taken from the literature (7). The slope of both curves is approximately the same in both cases. The data for the heterogeneous gel are slightly more



(U) Fig. 20 - Schematic Drawing of Modified Capillary Viscometer



(c) Fig. 21 - Apparent Viscosity vs. Shear Rate for Several Heterogeneous AlH₃-1451/N₂H₄ Gels and Emulsions



(c) Fig. 22 - Density vs. Temperature for Heterogeneous Gel with polyacrylamide Gelling Agent

scattered than for hydrazine, which could be caused by voids that are very difficult to prevent during the sample loading.

(C) The calculated theoretical value for the polyacrylamide heterogeneous gel, neglecting the effect of the gelling agent, is 1.18 cc./g. at 77°C. The datum from this density vs. temperature determination in a pycnometer is 1.095 cc./g. at 77°C. However, earlier measurements with the air comparison pycnometer averaged 1.16 cc./g. at 77°C. Measurements with the air comparison pycnometer are much less subject to error from voids, but it is not readily adaptable to wide range temperature control; thus, it was not used for these determinations.

3. Mechanical Stability (U)

(U) The heterogeneous gel with the polyacrylamide agent was mechanically stirred in two different modes to evaluate the mechanical stability of the gel. A vibration stability test and an acceleration stability test were conducted under the conditions specified by the contract requirements.

a. Vibration Stability (U)

(U) A vibration test was run on gelled propellant that contained 0.5% gelling agent. The test conditions were 2 hours at 5 g peak sinusoidal vibration cycled over a range of 50 to 500 cps. and 10 minutes at 20 g peak sinusoidal vibration at 500, 1000, and 2000 cps. The temperature for each test was 40°, 80°, and 120°F. The test caused no separation or settling of the gel as determined by visual inspection and by a gravimetric procedure.

(U) The equipment for the vibration test consisted of the following:

- Ling shaker Model A 280 plus power amplifier.
- Hewlett Packard wide range oscillator.
- Hewlett Packard electronic counter.
- Ling accelerometer normalizing amplifier.
- Endevco accelerometer Model 22210.
- Tektronix type 502 dual beam oscilloscope.
- Honeywell Brown recorder, temperature range
-50° to +150°C.
- Sample holder mount.

The sample temperature was manually controlled to $\pm 1^\circ\text{C}$ with a heating tape as a heat source and Dry Ice on the exterior of the sample holder mount for cooling.

(U) Each test was run on triplicate 10-gram samples in glass vials that were held in magnesium tubes in the sample holder mount. After the gel was vibrated under the specified conditions, approximately 1 gram was sampled from the top and bottom and placed in a capped plastic vial. The sample was weighed on an analytical balance to determine the complete sample weight. After drying

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under vacuum at ambient temperature for 48 hours to remove the N_2H_4 , the dried residue was reweighed to determine total solids in the sample. The percentages of solids in the top and the bottom of the sample were calculated to detect separation of the sample. The results, listed in Table XV, are within the experimental error of the test method and indicate no settling of the gel from the vibration tests. These results verify visual inspection of the gel after testing.

Table XV(U) Settling Rate of Vibrated Heterogeneous Propellant

<u>Vibration Test Conditions</u>		<u>% Solids in Sample</u>	
<u>Time, min.</u>	<u>Temp., °F.</u>	<u>Top</u>	<u>Bottom</u>
120	40	38.96	38.95
120	80	39.42	38.90
120	120	38.20	38.46
10	40	38.81	39.52
10	80	37.92	36.96
10	120	38.40	38.14

(U) The center portion of the 10-gram samples was tested for yield stress and compared to the control portion of untested gel from the same batch. The freshly vibrated gel apparently remained in a stressed state for several hours after the test, for the yield values were higher than the control (see Table XVI). However, vibrated gel that was allowed to stand for 24 hours after the test apparently "relaxed," for the yield stress was in the approximate range of the control gel. The control gel showed the usual yield stress during the first 48 hours of storage after mixing. The yield stress value then leveled out and stayed approximately constant.

Table XVI(U) Yield Stress of Vibrated Heterogeneous Propellant

<u>Elapsed Time After Gel Preparation, days</u>	<u>Yield Stress, dynes/cm.²</u>	
	<u>Control Gel</u>	<u>Tested Gel</u>
0	1635	--
1	1170	945
3	770	870
8	350	820
10	600	325 ^a
11	475	320 ^a

^aYield stress was tested long enough after vibration test to allow gel relaxation.

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b. Acceleration Stability (U)

(C) The mechanical stability of the heterogeneous polyacrylamide gels was tested under the specified acceleration conditions: 1 hour at 20 g load and 10 minutes at 90 g load (each test at 77°F). The yield stress needed to prevent separation under the stated acceleration loads was determined.

(C) A variable speed International Centrifuge Model EXD was used for the acceleration stability study. Several gels with a range of yield stress values were centrifuged in duplicate at the specified acceleration loading and temperature. The gels were visually inspected and then tested for separation by the method described in Section III.C.3.a. A gel with a low yield stress (475 dynes/cm.²) separated noticeably in both the 20 g and 90 g tests. The gravimetric test also showed considerable separation, (see Table XVII). A gel with a yield stress of 1000 dynes/cm.² withstood the acceleration test much better. No separation was visible and the gravimetric test showed only a trace of separation. Since earlier test gels with yield stress values as low as 700 dynes/cm.² were centrifuged with no visible separation, the data from these tests indicate that the yield stress of the heterogeneous propellant should be at least in the 700-1000 dynes/cm.² range or greater to meet the mechanical stability requirements.

Table XVII

(U) Effect of Yield Stress on Separation
Of Solids Under Acceleration

Yield Stress dynes/cm. ²	Change in Solids, % (Bottom Minus Top)	
	20 g, 1 hr.	90 g, 10 min.
1710	nil	nil
1000	0.3	0.8
475	17.7	29.1

4. Minimum Usable Temperature (U)

(U) The minimum usable temperature, i.e. the lowest temperature at which the gel is still liquid and pumpable, was determined by measuring the yield stress of the gel from 25°C to -2.5°C, which is below the freezing point of the gel. The minimum usable temperature was set at 0°C, the gel freezing point, as a result of this study.

(U) During this work, the yield stress was measured by the rising sphere rheometer and by the microcapillary rheometer. (See Appendix C for the two test methods). Greater precision of yield stress measurements at 25°C was observed with the microcapillary rheometer than with the rising sphere rheometer. Calibration data of the microcapillary rheometer with a homogeneous water gel were reproducible within 2%; whereas the rising sphere was only reproducible within 10%. In addition, yield stress values

determined by microcapillary are approximately twice as great as values measured by the rising sphere apparatus. An aluminized gel made with Carbopol-940, when tested with the microcapillary rheometer, showed yield stress of the same magnitude as comparable aluminized gels reported by Stanford Research Institute (9). Therefore, values from the microcapillary apparatus were judged to be more reliable than from the rising sphere rheometer. Since testing time and sample size are both considerably less and the precision of data much better, the microcapillary rheometer was used for yield stress measurements of gel and emulsion systems at 25°C. However, for temperatures below 10°C, problems were encountered with the microcapillary method. The yield stress data were widely scattered as if the gel began to shrink and/or adhere to the tube. In order to measure the yield stress below 10°C, the results obtained with the rising sphere rheometer were correlated with the results obtained with the microcapillary rheometer and a factor applied to values measured with the rising sphere to bring yield stress into line with the microcapillary values.

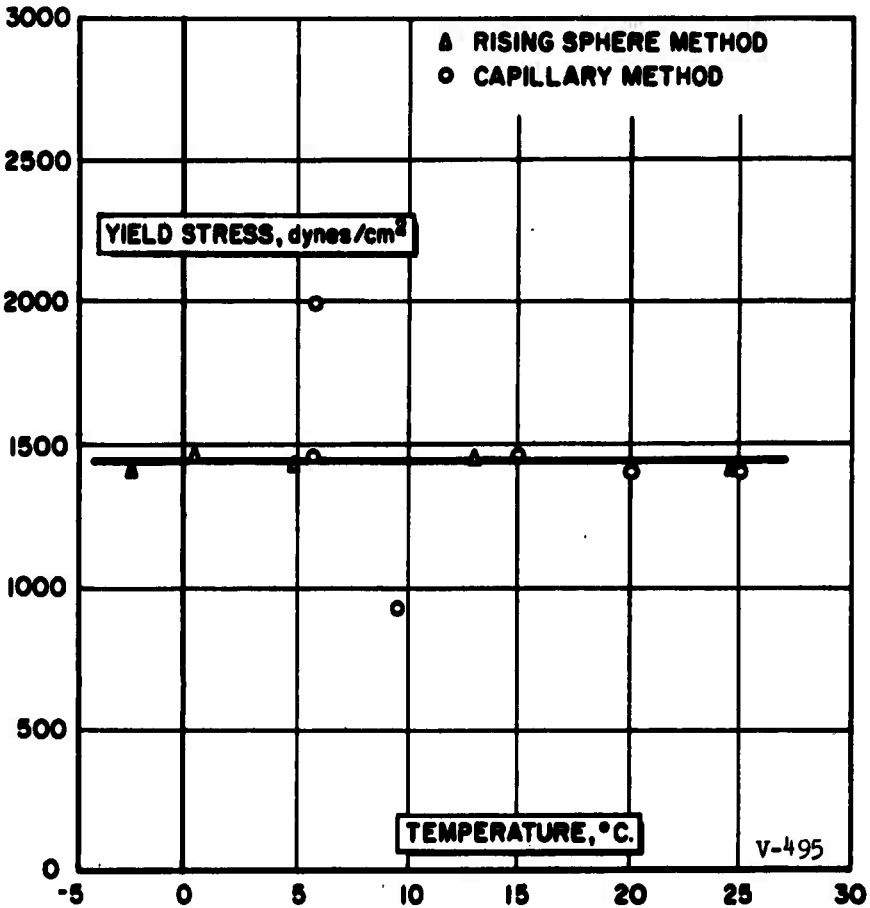
(C) The yield stress of the gel was measured over a range of temperatures with the rising sphere and adjusted to correspond to capillary data. As long as the gel was still in the liquid state (even though supercooled), the yield stress remained essentially constant (see Figure 23). Therefore, the minimum usable temperature is considered to be at or above the freezing point of 0°C.

5. Thermal Stability (U)

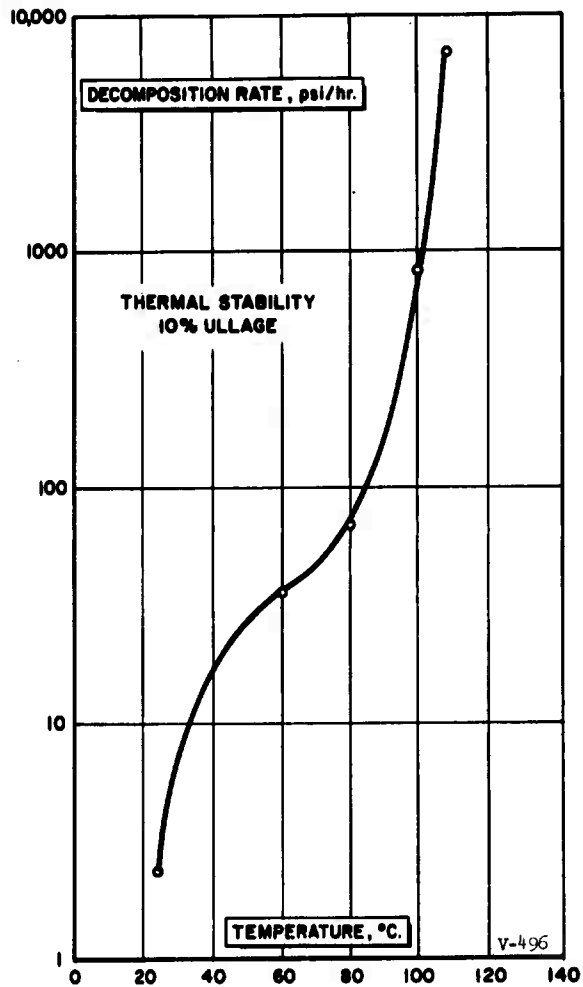
(U) The swelling rates of freshly prepared gels were evaluated from room temperature to boiling to determine the short range effect of thermal exposure on the gel. The data were converted to pressure rise (psig) per hour for a storage container with 10% ullage. Data were presented in Figure 24.

(U) The thermal stability tests were run in a 100 cc. heavy wall glass tube containing approximately 25 grams of freshly prepared gel. This tube was connected to a Heise gauge and mercury manometer for pressure measurement. The tube was submerged in a constant temperature bath. The pressure was recorded at minute intervals for about 30 minutes, until the sample equilibrated. Then the pressure was recorded as often as needed to obtain sufficient data, every 1-4 hours. The initial pressure rise during temperature equilibration was deducted from the total pressure rise. Swelling rate calculations were based on the steady state gas evolution during approximately the first 24 hours of the test. For temperatures below 60°C, the gas evolution decreased markedly after the first 24 hours that the sample was held at temperature. However, for temperatures above 60°C no decrease in gas evolution was seen. Indeed, at the boiling point, 114°C, the evolution began to increase rapidly after only two hours of testing.

(U) The gels were inspected for physical change after the tests. Voids had formed from gas evolution, but no separation of phases was seen. The yield stress was relatively unchanged. The physical stability of the tested gels was excellent during extended



(c) Fig. 23 - Data from the Minimum Usable Temperature Test of the Heterogeneous Propellant



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(C) Fig. 24 - Thermal Stability From Room Temperature to Boiling of Heterogeneous Propellant.

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ambient temperature storage after the test. However, the gels that had been exposed at 100° and 114°C gassed excessively during prolonged storage. These tests would indicate that the heterogeneous gels should not be exposed to temperatures in excess of 60°C (140°F) during handling and shipping, even for short periods of time.

D. PREPARATION OF HETEROGENEOUS GELLED PROPELLANT (U)

(U) Fifty pounds of AlH_3 -1451/ N_2H_4 heterogeneous propellant were prepared and shipped to AFRPL, Edwards, California. The individual ingredients and preparation procedure should be considered in specification preparation for the propellant. These items are discussed below.

1. Equipment Preparation (U)

(U) All glassware, containers and other equipment that contacts the gelled propellant or its ingredients should be passivated by the cleaning procedure that is outlined in Appendix C.II. to prevent contamination of the propellant.

2. Chemicals (U)

(U) Each of the chemicals that are ingredients in the propellant should meet the requirements outlined in the following section to ensure propellant stability and storability.

a. Hydrazine (U)

(C) The propellant grade anhydrous N_2H_4 (Spec MIL-P26536B) should contain no more than 1.0% and no less than 0.8% water. The aniline content should be no greater than 0.5%. The methods for N_2H_4 analysis are discussed in Section III.B.1.a.(2).

b. Polyacrylamide Gelling Agent (U)

(U) The polyacrylamide gelling agent, Dow proprietary compound, must compare to the agents CD 375-13-54 and/or ST-475-11-37B in molecular weight and degree of crosslinking. The amount of hydrolysis should be >0.1%. The agent is dried by an anhydrous methanol wash. The agent is washed in approximately three volumes of methanol for one volume of agent for 30 minutes with agitation in a closed container. The methanol is removed from the agent by filtration. This is repeated three times. The agent is then dried under vacuum and stored in a desiccator.

c. Aluminum Hydride-1451 (C)

(C) The Mg-doped AlH_3 -1451 must qualify in chemical purity and stability to be classified as propellant grade, with a preferred crystal size range of 80-200 μ . The hydride must be pre-treated to improve its stability in N_2H_4 . The n-butylamine treatment in III.B.2 is recommended. The treated hydride in

combination with N_2H_4 (40:60 ratio by weight) should evolve no more than 600 cc./lb. of gas after 500 hours at 60°C to produce a gelled propellant with a long-term gassing rate in the order of 1×10^{-3} cc./lb. min. at 25°C.

3. Gel Preparation (U)

(C) The gel is prepared by combining the AlH_3 -1451 and N_2H_4 and gradually adding the polyacrylamide gelling agent with moderate shear. The mixing equipment is constructed of glass or other materials acceptable for prolonged service with N_2H_4 . The preparation is outlined in the following example.

a. Mixing (U)

(C) The chemicals are handled under a dry nitrogen atmosphere. The mixer is a modified Sunbeam Mixmaster with Teflon-coated beaters that have two of the four blades removed. AlH_3 -1451 (800 grams) and N_2H_4 (1200 grams) are charged to the mixer and are agitated briefly to disperse and wet the solid. The gelling agent (12 grams) is added gradually during approximately 5 minutes by sprinkling it on the liquid surface with the mixing speed approximately 120 rpm. For an additional 25 minutes the gel is mixed for ten seconds out of every two minutes at a mixing speed of 60 rpm. The gel is discharged from the mixer by pouring with vibration.

b. Testing (U)

(C) Immediately after mixing, the yield stress is approximately 1200-1600 dynes/cm.². A final yield stress check should be run about 24 hours after mixing to determine if the gel is in the 700-1500 dynes/cm.² range that is sufficient to prevent settling of the AlH_3 -1451. The density of the gel should be measured as a check on the ingredient proportions.

c. Storage (U)

(U) The gel should be stored in dry, properly passivated pressure vessel with 10-15% ullage. If the gel is stored with an ullage greater than 15%, the N_2H_4 can evaporate and condense on the container walls which will eventually alter the gel composition. The 50 pounds of heterogeneous gel that was shipped to Edwards Air Force Base was loaded into stainless steel tanks furnished by the Air Force. The tanks had been purged with argon for 20 hours while held at 230°C to dry them after passivation. The gel was loaded into the cooled tanks under an inert atmosphere of dry nitrogen that was maintained in a glove bag fitted over the cylinder. The tanks had an ullage of 13-14% when filled with the gel.

SECTION IV

(U) RECOMMENDATIONS

- (U) 1. The ability to modify rheological properties of the hydrazine heterogeneous gels by chemical changes in the gelling agent is probably not limited to hydrazine. It is recommended that this technique be investigated with hydrazine derivatives and mixed hydrazine fuels where heterogeneous tactical systems are of interest.
- (C) 2. Pretreatment techniques for aluminum hydride have led to extremely stable neat material. The program in this regard was limited and should be further investigated to extend the usefulness of aluminum hydride in other systems. This in part is currently being studied under Contract F04611-68-C-0021. The use of aluminum hydride in other liquid carriers could also be investigated.
- (U) 3. Some physical properties of the heterogeneous system change with time, e.g., yield stress. This phenomenon is not fully understood and should be investigated further. It is felt that it is related to the rheology of the particular gelling agent, relaxation time, crosslink density, etc. Basic knowledge of this type could give better indication of performance in long-term storage under varying conditions.
- (U) 4. The parameters in large scale preparation of the heterogeneous system were not fully investigated in this program. Before large scale preparation is attempted, a program of study should be initiated to determine the effect of various preparation techniques on physical and chemical stability.
- (U) 5. It is not felt that the gassing rates presented in this study represent the maximum storage potential of the propellant. Further work in dilatometers designed for the gassing rate observed would better define the maximum stability potential.

SECTION V

(U) REFERENCES

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SECTION IV

APPENDIX A

I. GELLING AGENT SCREENING (U)

Table XVIII

(U) Gelling Agent Screening: Polyacrylamides^a

Agents	Solubility	Cohesive	Adhesive	Shear-Thinning	Compatibility
6047-17-1	Plus/minus	Minus	--	--	--
6047-16-3	Plus/minus	Minus	--	--	--
6047-11-1	Plus	Plus/minus	Plus	Minus	Plus
6047-15-1	Plus	Plus	Plus	Plus/minus	Plus
4955-10-1	Plus	Plus	Plus	Plus/minus	Plus
588-118	Plus	Plus/minus	Plus	Minus	Plus
97-17-1	Minus	Minus	--	--	Plus
92-17-2	Minus	Minus	--	--	Plus
92-42-1	Minus	Minus	--	--	Plus
92-42-2	Minus	Minus	--	--	Plus
92-42-3	Minus	Minus	--	--	Plus
92-42-4	Minus	Minus	--	--	Plus
Separan MGL	Plus	Minus	--	--	Plus
6047-18-1	Plus/minus	Minus	--	--	Plus
6047-17-2	Plus	Minus	--	--	Plus
ET-753	Plus	Minus	--	--	Plus
ET-728-2	Plus	Plus	Plus/minus	Plus	Plus/minus
Separan NP-20	Plus	Minus	--	--	Plus
Separan NP-10	Plus	Minus	--	--	Plus
6047-10	Plus	Plus/minus	Plus/minus	Plus	Plus

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Table XVIII (Contd.)
(U) Gelling Agent Screening: Polyacrylamides^a

Agents	Solubility	Cohesive	Adhesive	Shear-Thinning	Compatibility
6047-16-2	Plus	Minus	--	--	Plus
6047-16-1	Minus	Minus	--	--	Plus
ET-273A	Minus	Minus	--	--	Plus
Separan NP-20 (fine)	Plus	Minus	--	--	Plus
Mydel 550	Plus	Minus	--	--	Plus
Separan PG2	Plus	Minus	--	--	Plus
CR-70	Plus	Minus	--	--	Plus
Bonafix 11	Plus	Minus	--	--	Plus
E-206	Minus	Minus	--	--	Plus
Separan AP-10	Plus	Minus	--	--	Plus
Separan NP-10 FW	Plus	Minus	--	--	Plus
Separan MGL 300-187A	Plus	Minus	--	--	Plus
Separan NC-15	Plus	Minus	--	--	Plus
Gel Gard M [®]	Plus	Plus	Plus/Minus	Plus	Plus
P-250	Plus	Plus	Plus	Minus	Plus/Minus
Carbopol-940	Plus	Plus	Plus/Minus	Plus	Plus

^aBy qualitative examination: plus has the property; minus does not have the property.

APPENDIX A

Table XXIX

(U) Gelling Agent Screening: Polyacrylates^a

Agents	Salt Form	Solubility	Cohesive	Adhesive	Shear-Thinning	Compatibility
TEX-B No.:						
1008	Na	Minus	--	--	--	--
1008.1	Na	Minus	--	--	--	--
1008.2	Na	Minus	--	--	--	--
1008.3	NH ₄	Plus	Plus	Minus	Plus	Plus
1008.4	NH ₄	Plus	Plus	Minus	Plus	Plus
1008.5	NH ₄	Plus	Plus/minus	Minus	Plus	Minus
1008.6	NH ₄	Plus	Plus/minus	Minus	Plus	Plus
1008.7	Na	Plus	Plus/minus	Plus	Plus/minus	Plus
Carbopol-940	--	Plus	Plus	Plus/minus	Plus	Plus

^aBy qualitative examination: plus has the property; minus does not have the property.

APPENDIX A

Table XX

(U) Gelling Agent Screening: Miscellaneous^a

Agents	Solubility	Cohesive	Adhesive	Shear-Thinning	Compatibility
ARA	Plus	Minus	--	--	Plus
ET-435 H ⁺	Plus	Plus	Plus/minus	Plus	Plus
ET-435	Plus	Plus/minus	Plus/minus	Plus/minus	Plus
Nitrosol-250	Plus	Minus	Minus	Plus	Plus
Gantreg AN-169	Plus	Minus	--	--	Plus
90 HG 4,000	Plus/minus	Minus	--	--	Minus
DVB	Plus	Minus	--	--	--
Kelzan	Plus	Minus	--	--	--
PVO-E	Minus	Minus	--	--	--
PVBMA ⁺ Cl ⁻	Plus	Minus	--	--	--
ET-400-4	Plus	Minus	--	--	--
NORBAK®	Plus	Plus	Plus/minus	Plus/minus	Plus/minus
J-150	Plus	Plus	Plus	Minus	Plus
DMMA ⁺ SO ₄ ⁻	Plus	Minus	--	--	--

^aBy qualitative examination: plus has the property; minus does not have the property.

APPENDIX A

Table XXI

(U) Screening Results for Acrylamide/Acrylate Copolymers

Agent	Agent Conc., %	Ratio Amide/Acid	Added Cross- linker	Gel Characteristic	24 hrs. at 50°C.	Remarks
ST-475-6-110A	0.5	10/90	0	No gel	--	--
ST-475-6-110C	0.5	50/50	0	No gel	--	--
ST-475-6-110D	0.5	76-24	0	Adhesive	No change	--
ST-475-6-110E	0.5	90/10	0	Adhesive	Thinned	--
ST-475-9-38A	0.5	60/40	4X	Cohesive	No change	Effective to 0.25% agent.
ST-475-9-38C	0.5	60/40	20X	Cohesive	--	Thin at 0.25% agent.
ST-475-9-38B	0.5	60/40	40X	Cohesive	--	Thin at 0.25% agent.

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Table XXII
(U) Heterogeneous Gel Properties^a

Gel No.	Agent	Composition, %			Cohesive	Adhesive	Heterogeneous Phase
		Agent	N ₂ H ₄	AlH ₃			
1	Gel Gard M [®]	0.5	60	40	--	Moderate	Included
2	ST-475-9-38A	0.3	60	40	--	Slight	Excluded
3	ST-475-9-38A	0.165	60	40	--	Slight	Excluded
4	Tex-B 1008.3	0.4	60	40	--	Very	Included
5	Tex-B 1008.4	0.4	60	40	--	Moderate	Included
6	Tex-B 1008.9	0.42	60	40	--	Very	Included
7	Tex-B 1008.15	0.42	60	40	--	Very	Included
8	Tex-B 1008.15	0.42	60 ^b	40	--	Very	Included
9	Tex-B 1008.15	0.42	60	--	40 ^c	Moderate	Included
10	Tex-B 1008.16	0.45	60	40	--	V. Slight	Included
11	Tex-B 1008.16	0.25	60	40	--	Moderate	Included
12	Tex-B 1008.16	0.25	60 ^b	40	--	Slight	Excluded
13	Tex-B 1008.16	0.45	60 ^b	40	--	Slight	Included
14	Tex-B 1008.16	0.42	60	--	40 ^c	Very	Included
15	CMC(80) Agar-Agar(20)	0.42	60	40	--	Moderate	Included
16	CMC(80) Agar-Agar(20)	0.42	60	--	40 ^c	Very	Included
17	Carbopol-940	0.42	60	--	40 ^c	Moderate	Included

^aNo gassing observed in these formulations.

^bDistilled hydrazine: 0.1% H₂O; all other as-received: 0.8% H₂O.

^cRE-131 5 μ aluminum.

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II. EMULSIFYING AGENT SCREENING (U)

Table XIII
Properties of Ammonium Polycrylate Metastemous Propellant
Containing 10% Aluminum Hydride-1451 and 60% Hydrazine (C)

Agent	Concentration %	Gal Time min.	Cohesion	Ease of Shear Nr. 15 Needle	Flow	Density g./cc.	Centrifuge 10 min. at 180 g.	Yield Stress dyn/cm ²	Storage Stability	
Tex-B-1008.9	0.35	<3	V. good	Good	Not good	None	1.105	No separation	--	Poor
Tex-B-1008.15	0.42	<2	Sl. adhesive	Pair	Good	Slight	1.105	No separation	503	Good
Tex-B-1008.17	0.42	<4	Good	Good	Not good	Slight	--	--	--	Pair
Tex-B-1008.17	0.35	4-5	Good	Good	Good	V. slight	--	No separation	1642	Pair
Tex-B-1008.15/ ST-475-10-482(4:1)	0.42	<1	Good	Good	V. good	V. slight	--	No separation	1511	Good
CMC 787/Agar-Agar (4:1)	0.42	12-16 ^a	Adhesive	Pair	V. good	Good	--	Sl. separation	1654	Good

^aHours

Table XXIV

(U) Emulsifying Agent Screening Summary

Agents	Solubility			HLB ^a	Spreading Coefficient	Emulsion Type
	Water	NaH ₄	Decane			
Esters						
Tween 80	---	---	Insoluble	15.0	---	Reaction
Span 80	---	---	Soluble	4.3	---	Reaction
Tween 65	---	---	Soluble	---	---	Reaction
Hodag 150-S	---	---	Partially soluble	---	---	Reaction
Hodag 100-S	---	---	Insoluble	---	---	Reaction
Hodag 40-S	---	---	Partially soluble	---	---	Reaction
Pegosperser 600 MS	---	---	Insoluble	---	---	Reaction
Pegosperser 200 ML	---	---	Partially soluble	---	---	Reaction
Aldosperser L9	---	---	Insoluble	---	---	Reaction
P.E.G. ^b (6000) distearate	---	---	Insoluble	---	---	Reaction
P.E.G. (600) monooleate O	---	---	Insoluble	---	---	Reaction
P.E.G. (600) monolaurate	---	---	Partially soluble	---	---	Reaction
Ethers						
Ethosperser LA-23	---	---	---	---	---	O/W ^c
Ethosperser LA-4	---	---	---	---	---	Unstable
Brij 52	Insoluble	---	Soluble	3-6	Minus	Unstable
Brij 92	Partially soluble	---	Soluble	3-6	Minus	Unstable
Brij 96	Soluble	---	Partially soluble	13+	---	---
Renex 30	Soluble	---	Insoluble	13+	---	---
Atlas G-1690	Soluble	---	Insoluble	13+	---	---
Sterox SK	Partially soluble	---	Insoluble	8-10	---	---
Polytergent B-200	Partially soluble	---	Partially soluble	8-10	---	---
Tergitol NP-14	Partially soluble	---	Soluble	4-7	Minus	Unstable
Sulfated lauryl ether of tetra-ethylene glycol, Na salt	Soluble	---	---	13+	---	---
Alcohols and Phenols						
P.O.E. ^d lauryl alcohol (23 moles EtO)	Soluble	---	---	13+	---	---
P.O.E. oleyl alcohol (20 moles EtO)	Soluble	---	Partially soluble	13+	---	Unstable
Agrimul 70-B	Partially soluble	---	Partially soluble	8-10	---	---
P.O.E. tert-octylphenol (3 moles EtO)	Partially soluble	---	---	5-7	---	Unstable
Renex 648	Partially soluble	---	Soluble	8-10	Minus	---
Dowfax 9N4	Partially soluble	---	Soluble	6-8	Minus	Unstable
Dowfax 9N9	Soluble	Partially soluble	Partially soluble	13+	---	---
Hyonic PE 30	Partially soluble	---	Soluble	4-7	Minus	Unstable
Polytergent G-200	Partially soluble	---	Partially soluble	8-10	---	---

APPENDIX A

Table XXIV (Contd.)

(U) Emulsifying Agent Screening Summary

Agents	Solubility			HLB ^a	Spreading Coefficient	Emulsion Type
	Water	N ₂ H ₄	Decane			
Amines and Diamines						
P.O.E. oleyl amine	Partially soluble	---	Soluble	6-8	---	W/O ^c
Katapol PN-430	Soluble	---	Soluble	8-10	Minus	---
Armeen 2HT	Insoluble	---	Insoluble	1-4	---	Unstable
Ethomeen S-12	Partially soluble	---	Soluble	6-10	Minus	---
Atlas G-3763	Partially soluble	---	Soluble	8-10	Plus	---
Duomeen S	Insoluble	---	Partially soluble	3-6	Minus	Unstable
Formonyte 801	Insoluble	---	Soluble	6-8	Minus	---
Diam 26	Partially soluble	---	Partially soluble	6-10	---	---
Tetronic 704	Soluble	---	Insoluble	13+	---	---
N-Soya-ethylenediamine	Insoluble	---	---	3-6	---	Unstable
Triethanolamine oleate	Soluble	---	---	10-13	---	---
Amides						
Lauric acid monoethanolamide	Partially soluble	---	Insoluble	5-7	---	Unstable
Oleic acid monoisopropanolamide	Partially soluble	---	Insoluble	6-8	---	O/W
P.O.E. oleic amide	Partially soluble	---	Insoluble	8-10	---	Unstable
Ethomid C-15	Soluble	---	Insoluble	10-13	---	---
Prosol 1001A	Partially soluble	---	Insoluble	8-10	---	---
Sulfates						
Sodium oleyl sulfate	Soluble	---	---	10-13	---	---
Ammonium lauryl sulfate	Soluble	---	---	13+	---	---
Base 136B	Soluble	---	Insoluble	10-13	---	---
Sulfonates						
Atlas G-3300	Partially soluble	---	Soluble	11.7	Plus	Reaction
Calimulse DM	Partially soluble	---	Soluble	5-7	Plus	Reaction
Ninate 411	Soluble	Partially soluble	Soluble	9-11	Plus	Reaction
Emcol P10-57	Partially soluble	---	Soluble	8-10	Plus	Reaction
Tenlo 400	Soluble	---	Soluble	13+	Plus	Reaction
Complex Nitrogenous						
Alkaterge C	Partially soluble	---	---	6-8	---	---
Polyglycol 109-5	Insoluble	---	Insoluble	4-7	---	---
Sarkosyl O	Partially soluble	Soluble	Soluble	4-7	Plus	Reaction
Deriphat 160C	Soluble	---	Insoluble	13+	---	---
Hodag C-100-0	Insoluble	---	Partially soluble	3-6	Minus	W/O

APPENDIX A

Table XXIV (Contd.)

(U) Emulsifying Agent Screening Summary

Agents	Solubility		HLB ^a	Spreading Coefficient		Emulsion Type
	Water	N ₂ H ₄		Decane	Minus	
Hodag C-100-T	Insoluble	--	Partially soluble	3-6	W/O	
Substituted imidazolinium salt	Partially soluble	--	--	5-7	--	Unstable
Substituted imidazolinium salt	Partially soluble	--	--	--	--	Unstable
Blends						
Alttox 3402	Soluble	--	Insoluble	13+	--	--
Emcol H-83T	Partially soluble	--	Partially soluble	9-11	--	--
Emcol-H-700	Partially soluble	--	Partially soluble	9-11	--	--
Others						
Aluminum oleate	Insoluble	--	Insoluble	1-4	--	W/O
Ammonium stearate	Partially soluble	--	--	6-8	--	--
Ammonium leate	Soluble	--	--	8-10	--	--
Perfluoro surfactant	--	--	--	--	--	Unstable
Pluracol TP 1540	Partially soluble	--	Soluble	--	--	--
Sterotex	--	--	Insoluble	--	--	Unstable

^aHydrophile-lipophile balance.^bPolyethylene glycol.^cOil in water emulsion.^dPolyoxyethylene.^eWater in oil emulsion.

APPENDIX A

Table XXV

(U) Screening of Emulsifiers^a

Emulsifier	With Water	With Decane	With NaH_4 ^b	Spreading Coefficient	Hydrophile-Lipophile Balance
D-2800	Solution	Milky dispersion	Poor dispersion	Negative	13+
H-4279	Solution	Solution	Poor dispersion	Slightly negative	13+
H-4364	Solution	Solution	Poor dispersion	Very negative	13+
H-4422	Solution	Solution	Solution	Very negative	10-13
H-4423	Poor dispersion	Solution	Solution	Negative	3-8
H-4424	Milky dispersion	Poor dispersion	Partial solution	Slightly negative	6-8
H-4425A	Poor dispersion	Solution	Partial solution	Very negative	3-6
H-4425B	Poor dispersion	Solution	Partial solution	Very negative	3-6
H-4426A	Translucent gel	Solution	Solution	Negative	10-13
H-4426B	Translucent gel	Solution	Solution	Slightly negative	10-13
H-4427	Translucent gel	Solution	Solution	Negative	10-13
H-4428	Solution	Solution	Solution	Negative	13+

^aReceived from AFRPL.

^bAll samples gassed when added to hydrazine.

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APPENDIX B

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APPENDIX B

Table XXVI

(C) Stability and Analyses of Treated Heat Aluminum Hydride-1451 Samples

Sample Number	Hydride Treated	Treatment			Stability in NaOH Hrs. to Reach 0.1% at 60°C.	Analysis, %							Remarks	
		Liquid	% H ₂ O	Time, days		Temp., C.	O ₂	C	H	N	Na	Cl		
BHS 1-129-A	09236	--	--	--	--	520	0.33	0.15	9.92	0.18	1.18	0.23	0.08	Control
1-129-1	09236	N ₂ H ₄	0.8	12	25	~250	0.47	0.25	10.04	0.22	1.20	0.20	<.05	
1-129-2	09236	N ₂ H ₄	0.8	12	40	~280	0.53	0.15	10.07	0.18	1.15	0.16	0.030*	
39-1-4	09236	N ₂ H ₄	0.8	6	60	445	0.67	0.2	9.85	0.3	1.14	0.23	<.05	
1-137-1	09236	N ₂ H ₄	0.8	6	60	515	0.78	0.2	9.78	0.22	1.18	0.20	<.05	
1-129-6	09236	N ₂ H ₄	0.8	12	60	465	0.96	0.2	9.82	0.08	1.18	0.16	<.05	
1-148-4	09236	N ₂ H ₄	0.8	6	68-75	395	0.98	0.2	9.76	<.1	1.22	0.19	<.05	Soxhlet ext.
1-143-1	09236	N ₂ H ₄	0.8	6	60	595	1.04	0.2	9.85	0.30	1.17	0.19	0.039* <.05	S/L 40:120
39-1-5	09236	N ₂ H ₄	0.8	25	60	535	1.07	0.25	9.81	<.1	1.19	0.22	0.036*	S/L 40:30
1-129-3	09236	N ₂ H ₄	0.8	18	60	1090	1.22	0.2	9.84	0.30	1.18	0.17	<.05	
1-137-2	09236	N ₂ H ₄	3.2	6	60	500	2.41	0.2	9.56	0.16	1.13	0.20	<.05	
39-8	09236	n-Butylamine	1.81	6	60	995	0.92	0.2	9.83	0.18	1.20	0.22	0.092*	Stirred
39-7-4	09236	n-Butylamine	1.81	6	60	~1035	1.26	0.3	9.87	0.06	1.23	0.24	0.119*	
39-1-2	09236	n-Butylamine	2.08	18	60	~3600	1.54	0.45	9.76	0.4	1.09	0.22	0.094*	
1-143-1	09236	n-Butylamine	2.08	6	60	~1370	1.58	0.3	9.86	0.24	1.18	0.22	0.12* 0.1	
1-151	09236	n-Butylamine	2.08	6	60	610	1.91	0.3	9.72	<.1	1.21	0.21	<.05	Soxhlet ext.
39-1-1	09236	n-Butylamine	2.08	6	60	~1450	2.84	0.37	9.58	0.40	1.10	0.20	0.055* N ₂ H ₄ wash	
39-1-3	09236	iso-Butylamine	1.51	6	60	1600	1.14	0.25	9.78	0.30	1.13	0.23	0.115*	
39-7-1	09236	MEH	1	6	60	335	0.61	0.2	9.89	0.26	1.22	0.22	0.078*	
39-7-2	09236	MEH	1	1.0	6	395	1.08	0.4	9.84	0.13	1.21	0.24	0.134*	
39-7-3	09236	MEH	1	6	60	625	1.77	0.4	9.81	0.12	1.24	0.21	0.043*	Delayed work-up
1-137-5	09236	Benzene	<0.8	6	60	--	0.85	0.2	9.77	0.52	1.17	0.21	0.12	
1-137-3	09236	Benzene	0.8	6	60	745	1.74	0.2	9.77	0.19	1.15	0.22	0.13	
1-129-4	09236	Decane	0.8	12	60	300	2.05	0.2	9.81	0.02	1.15	0.18	0.11	
1-137-4	09236	Benzene	3.2	6	60	705	3.86	0.1	9.46	0.38	1.10	0.21	0.13	
1-129-5	09236	Decane	3.2	12	60	515	7.68	0.2	9.22	0.19	1.10	0.17	0.11	
1-148-3	09236	n-PrOH	0.68	6	60	360	0.68	0.2	9.82	<.1	1.27	0.18	<.05	
1-143-2	09236	EtAC	0.46	6	60	435	0.86	0.2	9.91	0.07	1.16	0.22	0.15* 0.08	
1-143-5	09236	EtOH	0.46	6	60	860	0.87	0.2	9.98	0.38	1.15	0.20	0.094* <.05	
1-143-6	09236	EtOH	1.46	6	60	970	1.30	0.4	10.04	0.20	1.17	0.21	0.099* 0.08	
1-148-1	09236	THF	0.1	6	60	~410	3.85	1.18	9.16	<.1	1.33	0.15	0.07	
BHS-39-16-1	Blend	--	--	--	--	230	0.43	0.86	9.97	--	1.14	0.19	0.09	Control
1298-34-2	Blend (#1)	n-Butylamine	1.81	17	60	3570	0.89	0.3	9.75	0.6	0.97	0.17	0.049*	Stirred (3/4 lb.)
39-12-3	Blend	n-Butylamine	--	9	60	765	1.52	0.43	9.81	0.13	0.94	0.19	0.023*	Stirred (3/4 lb.)
39-12-5	Blend	n-Butylamine	--	17	60	1425	1.74	0.36	9.74	0.12	0.92	0.19	0.036*	Stirred (3/4 lb.)

*Analysis by neutron activation; all other analyses by standard chemical methods.

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APPENDIX C

I. TALIANI METHOD TO TEST THERMAL STABILITY (U)

(U) The Taliani method equipment consists of a Pyrex glass sample tube, connected to a mercury manometer with a glass capillary tube containing a three-way stopcock. All glassware volumes have been calibrated accurately by weighing the amount of mercury required to fill the assembled glassware. The total volumes of the assembled units range from 5.16 to 5.86 ml.

(U) A standard cleaning procedure which is listed in the following section has been adopted for the Taliani glassware. This procedure essentially consists of immersion in caustic and acid cleaning batches, passivation with 50% N_2H_4 in H_2O , distilled water rinse, and drying for 16 hours at 120°C .

(C) Samples containing AlH_3 -1451 and hydrazine are prepared by weighing 0.40 g. of the hydride into the sample tube and adding 0.60 ml. N_2H_4 with a 1.00 ml. syringe. (Gelled samples will be prepared in other containers in the dry box and weighed into the Taliani tube.) To simulate contact with an aluminum storage tank, a piece of Type 2014 aluminum is included in the Taliani tubes. All loading operations are carried out in a dry box under inert nitrogen atmosphere. Silicone grease is used on all standard tapered joints. The glassware is assembled in the dry box, the stopcock is closed and the assembled unit is then removed from the dry box and placed on the Taliani apparatus. One half hour is allowed for the sample to come to thermal equilibrium with the constant temperature bath before manometer readings are taken. Readings are then taken periodically as necessary and the gas pressure in the tubes is relieved approximately every 48 hours, or as needed to prevent excessive pressure buildup in the apparatus.

(C) The results of the accelerated compatibility studies at elevated temperatures are presented as volume of gas (cc.) (corrected to 25°C and 1 atm.) produced per minute per pound of propellant containing 40% AlH_3 -1451. A scale showing percent decomposition of AlH_3 -1451 is included in the graphs to enable easy reference to standard AlH_3 -1451 stability data. These values assume that all gas is generated by hydride decomposition.

II. TALIANI GLASSWARE CLEANING PROCEDURE (U)

- (U)
1. Remove decomposed solids from the Taliani sample tube and rinse with water.
 2. Use a test tube brush to loosen remaining solids in the sample tube and rinse with water.
 3. Rinse glassware with acetone.
 4. Immerse glassware in Chlorothene® bath for at least 16 hours.

5. Rinse glassware with acetone.
6. Immerse glassware in a caustic bath for at least 16 hours.
7. Rinse glassware with water.
8. Immerse glassware in a chromic acid bath for at least 16 hours.
9. Rinse glassware with water.
10. Rinse glassware with distilled water.
11. Immerse glassware in a 50% N_2H_4 in H_2O solution for at least 16 hours.
12. Rinse glassware with distilled water.
13. Dry glassware in an oven at $120^\circ C$ for at least 16 hours.

III. GLASS DILATOMETER (4) (U)

(U) The equipment for the glass dilatometer thermal stability test consists of an all Pyrex glass system which is a sample chamber attached to a capillary manometer that is fitted with an expansion chamber, (see Figure 25). The sample bulb is calibrated accurately by weighing the amount of mercury that is required to fill the chamber to the joint between the chamber and the overhead tubing.

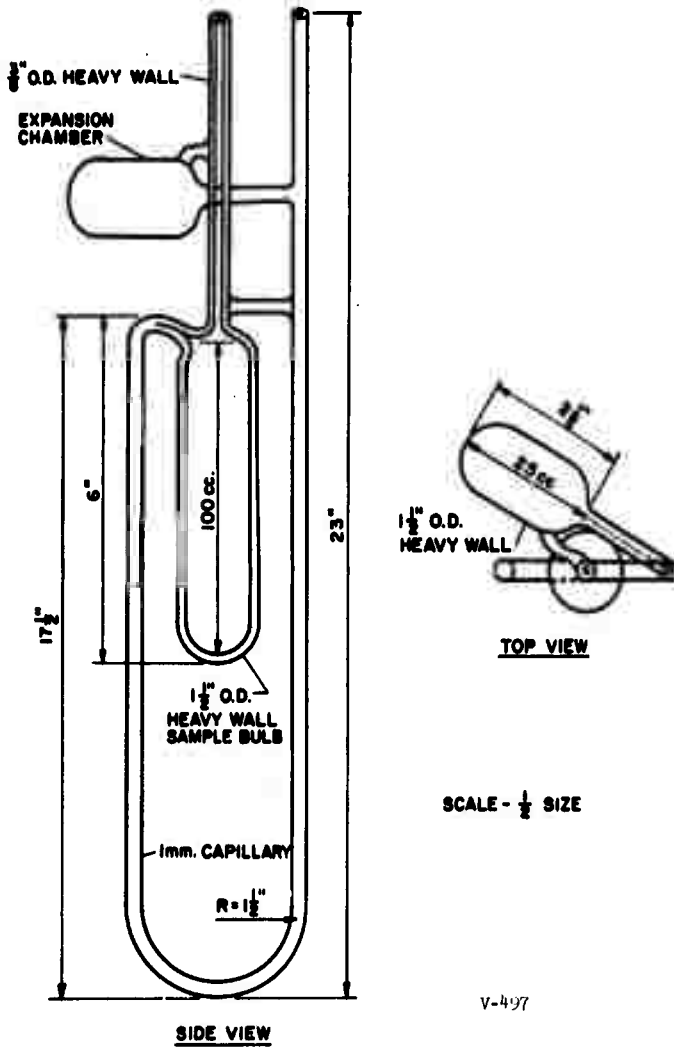
(U) The unit is cleaned by the standard cleaning process, Appendix C, Section II. The dilatometer unit plus syringe caps on the tubing ends is weighed before placing in the dry box.

(U) The gelled sample is prepared in another container in a dry box and is then transferred to the dilatometer, still under the inert nitrogen atmosphere of the dry box. Approximately 100 cc. of sample is placed in the sample bulb through the glass tubing with a 100 cc. syringe equipped with a very long Nr. 15 needle. The dilatometer is capped and is removed from the dry box. The unit is reweighed to determine the amount of gel that is being tested.

(U) Mercury is introduced into the capillary with a syringe and long needle and the unit is then sealed after cooling in an ice bath. A meter stick is attached to the longer capillary section, the dilatometer is placed in a controlled temperature chamber to equilibrate. The test is begun when the levels of mercury in the manometer reach equilibrium (8-16 hours).

(C) The results of the stability test are presented as volume of gas (cc.) (corrected to $25^\circ C$ and 1 atm.) produced per

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(U) Fig. 25 - Glass Dilatometer

minute per pound of propellant containing 40% AlH_3 -1451. A scale showing percent decomposition of AlH_3 -1451 is included in the graphs to enable easy reference to standard AlH_3 -1451 stability data. These values assume that all gas is generated by hydride decomposition.

IV. DENSITY MEASUREMENT (U)

(U) The density of the propellant was measured by a pycnometric technique utilizing a layer of mineral oil to adjust to a standard volume. Mineral oil is added to a weighed sample of propellant in a ground-glass stoppered, 25-ml. volumetric flask to adjust the volume to the calibration mark. The standard volume of the flask, less the volume occupied by the propellant sample, is the volume used to calculate the sample density. The precision and uncertainty among sample measurements are 0.003 g./cc. The density of the propellant is determined in accordance with Items A through B below with the following equipment:

- (a) Flask, volumetric, 25 ml. calibrated at 77°F (25°C.) with standard ground-glass stoppers, 3 required.
- (b) Water bath, temperature regulated at 77°F \pm 0.2°F (25°C)
- (c) Analytical balance, sensitivity 0.5 mg. (a rapid-weighing Mettler or Sartorius balance is recommended).
- (d) Eye dropper, common laboratory type.
- (e) Mineral oil, accurately measured density at 77°F. (25°C), one quart required. Nujol, from Plough, Inc., Los Angeles California.

A. Preparation (U)

(U) Thoroughly clean and dry the 25-ml. volumetric (density) flasks, including new flasks. The standard chromic acid cleaning solution is recommended, followed by five distilled water rinses, two rinses with methanol, and drying in oven or with a stream of gaseous nitrogen.

(U) Immediately prior to use, number the three density flasks and stoppers, purge with gaseous nitrogen and stopper each. Lubricant shall not be used with the glass stopper.

B. Procedure (U)

(U) Weigh the empty, stoppered density flasks on an analytical balance and record the weight of each flask as the tare weight, W_{T_1} .

(U) Place the propellant sample in the bottom of the density flask with a pipette, or allow to flow in under pressure through a 1/4 inch stainless steel tube inserted down the neck of the flask.

The sample size shall be sufficient to fill about three-fourths of the body of the flask. The recommended technique for admitting the sample into the flask is to extend the tube close to the bottom, and allow material to slowly flow out, and carefully raise the tube so the tube end is constantly at the surface of the material in the flask. This technique helps to minimize entrapped bubbles in the sample and it ensures that the outside of the delivery tube is not covered with sample material that can rub off onto the neck of the density flask and contribute to a volume error. When material accidentally contacts the neck of the flask, remove material with a cotton-dipped swab. Stopper the density flasks immediately after filling.

(U) Weigh the density flask containing samples and record the weights as tare plus sample weight, W_{TS} .

(U) Add mineral oil on top of the sample with an eye dropper to a level about 5 mm. beneath the calibration mark, and stopper the flask. Wipe the outside of the eye dropper with a paper tissue each time before it is inserted into the neck of the flask to prevent oil from rubbing off the dropper onto the neck of the flask above the calibration mark. Immerse the density flasks to the level of the calibration mark in a water bath regulated at $77^{\circ}\text{F} \pm 0.2^{\circ}\text{F}$ ($25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$).

(U) After two hours, remove the flasks from the water bath and, with an eye dropper, immediately add mineral oil dropwise to the contents to adjust the level to the calibration mark. Stopper the flask.

(U) Weigh the density flasks for the third time, and record the weight of the flask plus sample plus mineral oil at W_{TSO} .

C. Cleaning (U)

(U) Purge the density flasks with water through a 1/4-inch tube inserted through the flask neck. The flushing water will carry the bulk of the sample out of the flask, and the residue can be easily removed after adding a proper solvent to the flask to break the gel or emulsion. Caution: Waste propellant samples shall be combined with at least 10 volumes of water and always stored in an open container prior to disposal.

D. Calculations (U)

(U) Calculate the density of the propellant samples with the following equations:

$$\text{Volume of mineral oil, cc.} = \frac{W_{TSO} - W_{TS}}{d_o}$$

$$\text{Sample density, g./cc.} = \frac{(W_{TS} - W_T)}{(25.00 - \text{vol. of min. oil})}$$

Where: W_{TF} , g. = Tare weight of density flask.

W_{TFS} , g. = Weight of density flask plus sample.

W_{TFSO} , g. = Weight of density flask plus sample plus mineral oil.

d_o , g./cc. = Density 77°F (25°C) of mineral oil.

(U) Calculate sample densities to four significant figures. Report the arithmetic mean of the three sample densities as the measured density, 77°F (25°C), g./cc.

(U) The precision of the three measurements (average deviation from the mean) is obtained by totaling the difference of each from the arithmetic mean and dividing the sum by three. The precision shall be affixed within parentheses to the reported measured density.

V. YIELD STRESS MEASUREMENTS (U)

(U) Yield stress was determined by two methods, with the microcapillary and rising sphere rheometers.

A. Microcapillary Rheometer (U)

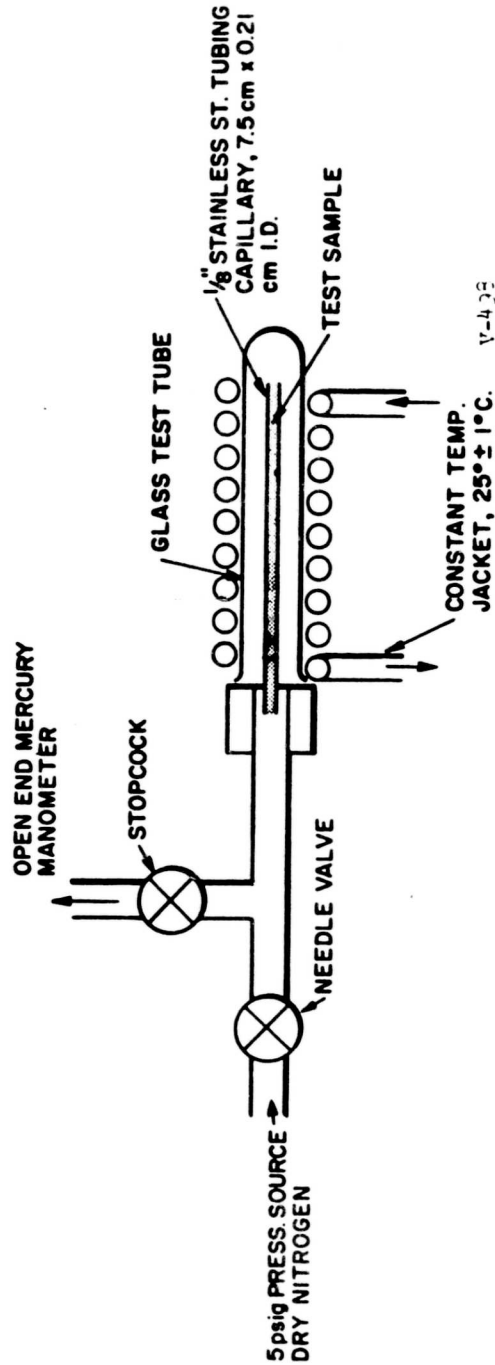
(U) For selective screening and most final characterizations, yield stress was determined with the microcapillary rheometer (see Figure 26).

(U) The sample is loaded into a 5-ml. syringe. The syringe is coupled to the stainless steel capillary with a short piece of plastic tubing (1-2 cm.). The sample is transferred from the syringe to the capillary. After the syringe is separated from the capillary, excess gel is cleaned from the ends of the capillary so that the sample is flush with the ends.

(U) The capillary is attached to the pressure source. Pressure (0-5 psig.) is placed on the end of the capillary in small increments. The end of the capillary that is open to atmospheric pressure is observed for the first movement of the sample in flow. The manometer stopcock is closed when movement is detected. The pressure is read from the manometer and the yield stress is calculated using the geometry of the capillary. The yield stress (σ) is equal to the differential pressure (Δp) across the capillary multiplied by the capillary radius (R) and divided by twice the capillary length (L). $\sigma = \Delta p R / 2L$.

B. Rising Sphere Rheometer (U)

(U) Yield values in liquids and gels can be determined by shearing the material at different rates in a suitably designed rheometer and measuring the accompanying shear stress. A flow



(U) Fig. 26 - Schematic Diagram of Microcapillary Rheometer for Yield Stress Determination

curve is then constructed by plotting the rate of shear against the shear stress. If the material possesses a yield value, extrapolation of the flow curve to a zero rate of shear intersects the stress axis at a point away from the origin. This point is taken as the yield value of the material.

(U) The rising sphere rheometer measures the yield stress because it is believed that it applies a stress to the sample under static conditions or at such a small rate of strain that static conditions are approached.

(U) The rising sphere method, originally developed by McVean and Mattocks (8) for viscoelastic liquids, consists essentially of measuring the force required to pull a sphere of known diameter through the test material. A stainless steel sphere is used to strain a gel sample to the limit at which the gel structure yields and the flow condition commences. The strain force applied from the surface of the sphere is measured by a strain gauge, and the output is recorded on a strip chart. A photograph of the assembled equipment is shown in Figure 27.

(U) A sample of adequate size of the material to be tested is prepared and placed into a suitable container. The container is designed to reduce or eliminate the evaporation of the solvent, and maintain an inert gas over the sample, and allow the yield stress to be measured. The sample should be measured at a constant temperature of about 25°C, controlled to ±0.1°C, and maintained by means of a constant temperature bath or other suitable equipment.

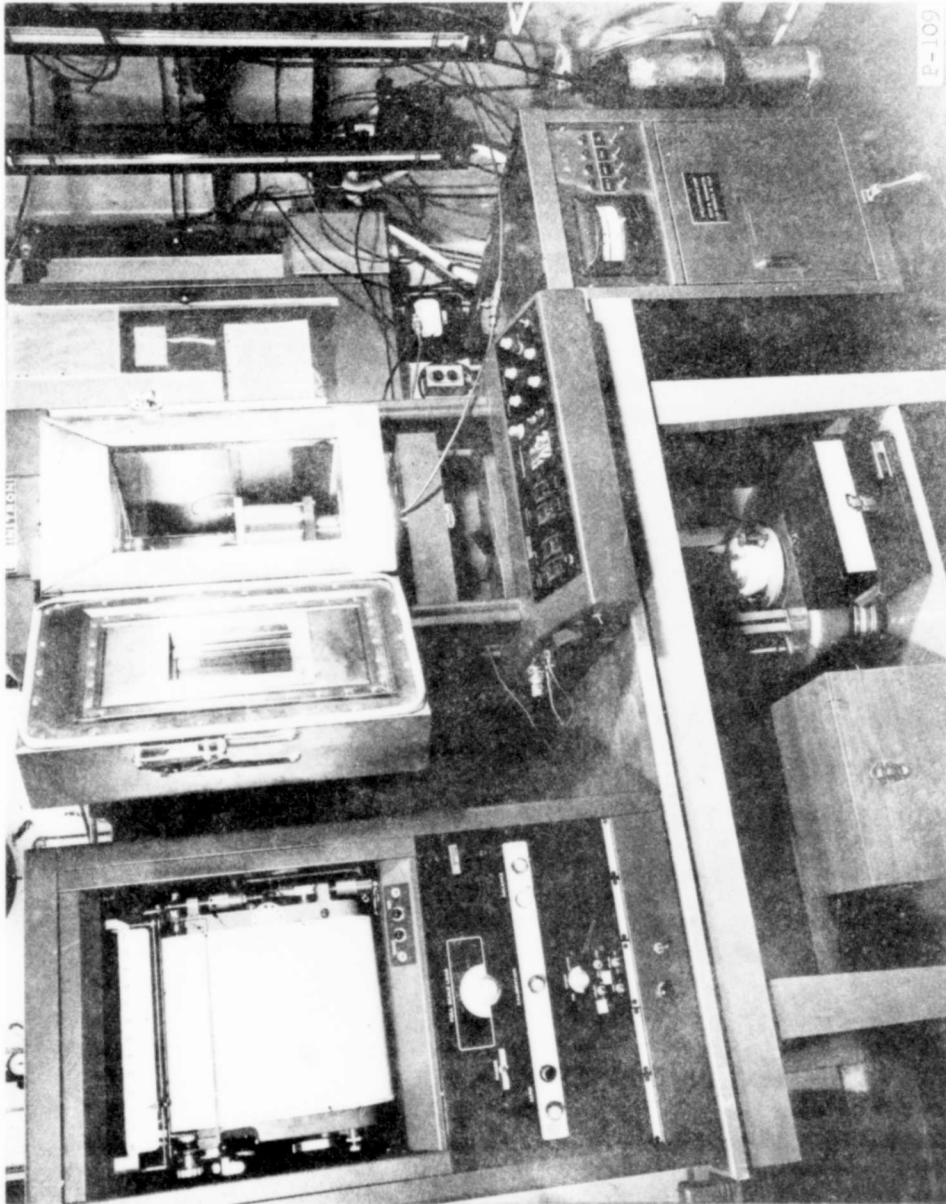
(U) The sphere is centered within the test material, while being supported from the strain gauge; to assist in the alignment of the sample, sphere, and strain gauge, positioning jigs can be used. All measurements begin after the sphere is raised about 1/2 inch above the bottom of the sample and left at this position for a minimum of 15 minutes.

(U) The sphere is then raised by means of a calibrated Instron Tester or other suitable device through the sample at a constant rate of 2.3×10^{-3} cm./sec. The restraining force on the sphere is measured. When a steady rate of shear (as witnessed by a leveling off of the force reading) has been achieved, the movement of the sphere can be stopped. Another rest period with additional measurements may follow. The shear rate is plotted against the stress and the curve extrapolated from the low shear rate end to zero shear.

(U) The maximum strain force, F , in grams, is used in the calculations of yield stress. The "corrected weight" of the sphere is calculated by subtracting the buoyancy effect of the sample on the sphere from the weight of the sphere in air. Corrected weight, gm. = (Wt. of sphere, gm.) - (Volume of sphere, cm.³) x density of sample, gm./cm.³.

Yield stress, dynes/cm.² = $\frac{(F - \text{Corr. Wt.}) \text{ gm.} \times 980 \text{ dynes/gm.}}{\text{Surface Area of Sphere, cm.}^2}$

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(U) Fig. 27 - Photograph of Instron Tester and Sample Holder

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13. ABSTRACT In an integrated program, a highly promising heterogeneous metallized propellant of LMH-1/ N_2H_4 , which is stable, storable and has desirable rheological properties has been developed. Chemical stability and physical integrity, combined with ease of preparation, make this system especially attractive. <p>The thermal stability and gas generation characteristics of LMH-1/N_2H_4 formulations were studied and one-year storability data were obtained. Major advances in LMH-1 technology have produced very substantial improvements in its stability. However, the stability of the best LMH-1 has been found to further enhanced by propellant grade hydrazine. Pretreatment of LMH-1 with n-butylamine at controlled temperature and moisture conditions have been found to be effective in minimizing initial gas generation and in long-term stabilization of LMH-1 in hydrazine formulations. A wide variety of gel and emulsions systems was investigated, which led to the selection of polyacrylamides for the heterogeneous system. This gelling agent in combination with 40% LMH-1 and 60% hydrazine produced a thixotropic heterogeneous propellant which exhibited a suitable yield stress and retained excellent physical integrity under vibrational and gravitational forces. The cohesive propellant developed was found to possess engineering properties which are desirable in heterogeneous propellants. Fifty pounds of propellant was prepared and sent to the AFRPL for Air Force in-house performance evaluation.</p>		

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